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Arias Calvo

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Turning biowaste into bio-materials and bio-active products: A domain of circular economy

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TESE DE DOUTORAMENTO

TURNING BIOWASTE INTO BIO-MATERIALS AND BIO-ACTIVE PRODUCTS: A DOMAIN OF CIRCULAR ECONOMY

Ana Arias Calvo

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Resumo

O obxectivo principal desta tese de doutoramento é a avaliación do potencial das biorefinerías e os esquemas de produción biotecnolóxica que utilizan fluxos de residuos desde as perspectivas da sustentabilidade e a circularidade. Para tal fin propuxéronse varias estratexias de valorización de residuos, enmarcadas nos sectores agroindustrial, forestal e da industria alimentaria, co obxectivo de obter unha gama de produtos de valor engadido: bioadhesivos para madeira, antimicrobianos, antioxidantes e bioenvases activos. A importancia deste tema baséase fundamentalmente no feito de que na actualidade resulta problemático xestionar axeitadamente a enorme cantidade de residuos que se xeran anualmente, que crece ano a ano, debido fundamentalmente ao aumento da poboación e á demanda de bens e servizos. Este feito supón importantes impactos ambientais que poden afectar tanto ao medio ambiente como á saúde humana, tendo en conta, por exemplo, as emisións asociadas á xestión de vertedoiros (é dicir, gases de efecto invernadoiro, lixiviados, etc.). Ademais, e quizais igual de importante, é o feito de que algúns destes residuos poderían potencialmente ser utilizados como materias primas para biorefinerías, dado o seu contido, por exemplo, en antioxidantes, azucres fermentables ou as súas propiedades fisicoquímicas. Para iso, os escenarios que se ofrecen nesta tese poden axudar a abordar estes problemas e a optar por estratexias de xestión e valorización de residuos máis adecuadas en materia de sustentabilidade e economía circular.

Na ***Sección I*** e na ***Sección II***, descríbese e discútese unha introdución dos principais temas relacionados coa valorización dos fluxos de residuos, xunto coas súas principais limitacións de xestión e impactos medioambientais. Por outra banda, é tamén neste apartado da tese no que se describen as principais metodoloxías empregadas para a análise dos escenarios: o Análise do Ciclo de Vida (ACV) como nexo de unión entre todos os capítulos e apartados, co obxectivo de analizar as cargas ambientais e perfís dos escenarios, estudo tecnoeconómico, para determinar a viabilidade económica das alternativas de valorización propostas, e a ecoeficiencia, para estudar a interrelación entre as perspectivas económica e ambiental co fin de seleccionar os mellores escenarios produtivos.

Sección III. *Bioadhesivos libres de formaldehido para paneis a base de madeira*

Esta sección ofrece adhesivos alternativos libres formaldehido para o sector de paneis de madeira empregando tanto fluxos lignocelulósicos, a base de taninos como residuais agroalimentarios. Concretamente, os fluxos de residuos que se valorizan son: lignina Kraft, procedente do proceso de pulpeo Kraft, Lignina Organosolv, obtida pola pasta Organosolv, taninos (**Capítulo 5**), obtidos principalmente polo descortizado e procesamento da madeira, a soia, como residuo procedente da transformación do cultivo de soia para a súa posterior produción, e o almidón (**Capítulo 6**), obtido pola valorización dos residuos de millo.

Para poder dispor de todos os datos necesarios para levar a cabo a metodoloxía ACV, plantéase un modelo de produción a gran escala dos bioadhesivos, tendo en conta a capacidade de produción dos sintéticos, co fin de proporcionar unha comparación a un nivel de produción análogo. Ademais do ACV, realizase un estudo de impacto a nivel dos límites planetarios, un paso máis na identificación da fortaleza dun escenario de base biolóxica particular dende o punto de vista ambiental. Con este enfoque, que se desenvolve no **Capítulo 7**, proporcionase unha visión máis global da potencialidade dos bioadhesivos, tendo en conta os límites de dano establecido polos límites planetarios.

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Capítulo 5. Bioadhesivos derivados de correntes residuais lignocelulósicas, forestais e da industria do procesado de papel.

O uso da lignina como recurso para a produción de bioadhesivos require unha etapa de funcionalización/activación para favorecer a reacción cos axentes de reticulación necesarios para a formulación final do adhesivo. Este paso de activación pódese levar a cabo por diferentes métodos, entre os que a glioxalación é un dos máis utilizados na literatura. Non obstante, observouse que este paso de funcionalización utilizando glioxal como axente de activación é moi prexudicial para o medio ambiente, principalmente pola cantidade de enerxía necesaria para esta etapa do proceso, que é o principal punto quente identificado. De feito, a achega eléctrica sobre o perfil ambiental desta primeira etapa é superior ao 80% para, principalmente, todas as categorías de impacto. Isto resulta nunha contribución ambiental da lignina no perfil de formulación do bioadhesivo superior ao 60% na maioría das categorías de impacto ambiental. Este feito conleva, en certa medida, a redución da potencialidade da lignina como recurso biolóxico.

Dado o alto impacto da glioxalación, desenvolveuse un proceso de funcionalización alternativo, mediante o uso de carbonato de dimetilo (DMC), proporcionando así un bioadhesivo de lignina libre de isocianatos, con cargas ambientais reducidas en comparación coa activación mediante glioxal. Este efecto de mellora demostrouse a partir dos valores de impacto obtidos tras o desenvolvemento da metodoloxía ACV. Concretamente, en tres categorías de impacto obsérvase unha redución máis notable, na de cambio climático, na ecotoxicidade terrestre e no esgotamento de recursos fósiles.

Co fin de ofrecer escenarios alternativos de bioadhesivos, baixo o enfoque de intentar mellorar a súa perspectiva ambiental, realízanse unha análise de sensibilidade arredor das variables de proceso con maior contribución ambiental. Observouse que a redución da demanda enerxética, así como a aposta polo uso de enerxías renovables, son as opcións coas que se consegue unha mellora máis notable das cargas ambientais obtidas. Por outra banda, outra conclusión á que se chega é que o impacto dos produtos químicos utilizados na formulación non é tan elevado, agás no caso da hexametilendiamina, onde se observa un importante impacto tanto no perfil ambiental.

Tamén se avalían os taninos condensados de lascas de cortiza mediante a realización de cinco escenarios de bioadhesivos, diferenciados principalmente polo tipo de axente de reticulación utilizado para a formulación final do bioadhesivo. O proceso implica a necesidade de desenvolver dúas etapas principais: a produción do tanino condensado e a reticulación co axente químico adecuado. Fronte ao que ocorreu coa activación da lignina, a etapa de condensación do tanino para favorecer a súa funcionalización non é tan impactante, de feito, a súa carga ambiental sobre os perfís obtidos non pasa dun 20-30%, o que favorece o potencial deste recurso biolóxico na formulación de adhesivos para madeira. Este feito demóstrase mediante a metodoloxía ACV, coa que se observa que, efectivamente, as cargas ambientais obtidas para os bioadhesivos a base de taninos son sensiblemente inferiores ás da lignina, coa excepción da alternativa do bioadhesivo de Organosolv libre de isocianatos, que teñen puntuacións análogas.

Os escenarios de sensibilidade dos bioadhesivos a base de taninos baséanse tanto na redución das necesidades enerxéticas como na redución da dose química, xa que nestes casos, algúns axentes químicos teñen certamente unha importante afectación ao perfil. As puntuacións obtidas mostraron que o uso de carbonato de etilo en lugar do carbonato de dimetilo implica

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realmente un beneficio importante, acadando valores de redución de impacto que poderían ascender a máis do 80% en categorías como acidificación e eutrofización, mentres que a redución da enerxía consumida proporciona unha mellora dos escenarios nun 20% de redución na maioría das categorías de impacto consideradas.

En canto á mellor alternativa para os bioadhesivos de taninos, segundo as puntuacións obtidas polo desenvolvemento da metodoloxía ACV, obsérvase que a utilización da hexametilendiamina como axente de reticulación é a que alcanza as menores cargas ambientais na meirande parte das categorías de impacto, con excepción do quecemento global, a ecotoxicidade e a escaseza de recursos fósiles, dadas as necesidades de electricidade e vapor, máis elevadas en comparación co resto de escenarios. Non obstante, ao valorar as alternativas mediante o método ReCiPe EndPoint, comprobouse que non só o citado bioadhesivo, senón que todos eles acadaron un potencial de dano e un único valor de puntuación inferior aos da resina sintética PF e, no caso do tanino reticulado con paraformaldehido, glioxal e hexamina, menor tamén en comparación coas resinas urea-formaldehido e melamina-urea-formaldehido, as máis utilizadas no sector de paneis de madeira.

Capítulo 6. Bioadhesivos obtidos a partir de residuos da industria agroalimentaria.

Buscando o uso da soia como materia prima para a produción de bioadhesivos, consideráronse dúas alternativas principais, o uso directo de fariña de soia ou o desenvolvemento dunha etapa de pretratamento para obter de proteína de soia, con calidade de adhesión e propiedades mecánicas melloradas para posteriormente reaccionar cos axentes químicos adecuados, co obxectivo de acadar características de adhesión similares ás das resinas sintéticas comúns (é dicir, calidade estrutural do taboleiro, tolerancia á humidade, etc.).

As propiedades de adherencia melloradas conseguidas pola extracción de proteínas para a fariña de soia tamén proporcionan resultados beneficiosos dada a súa implicación ao perfil ambiental, que é análoga, ou nalgúns casos, lixeiramente inferior á do uso da fariña de soia para algunhas das categorías de impacto, con excepción da categoría de impacto da eutrofización mariña, xa que empregar fariña ou proteína de soia non afecta sobre a contribución ambiental.

En canto aos principais contribuíntes dos perfís ambientais obtidos, con excepción da alternativa de proteína de soia reticulada con resina de tanino, na que a electricidade é o principal punto quente, os axentes de reticulación utilizados para a formulación dos bioadhesivos son os mais impactantes, acadando valores máximos de influencia do 60% ao 90% para as alternativas de fariña de soia, e do 50% ao 70% para as de proteína de soia. As categorías de impacto máis afectadas por isto son as relacionadas coa acidificación, a eutrofización e a saúde humana.

Outra alternativa baixo análise foi o uso de almidón, que require unha etapa de pretratamento para a súa funcionalización, igual que ocorreu co recurso de lignina, o uso directo non é efectivo para ser utilizado para a formulación de bioadhesivos. Con esta primeira fase de activación fórmase un maior número de centros activos, o que implica un maior rendemento na fase de reticulación, e conséguese unha redución da viscosidade, co que se conseguen mellores propiedades mecánicas adhesivas. Para iso, consideráronse dúas principais alternativas de pretratamento: a hidrólise do almidón e a oxidación dos grupos hidroxilo primarios e secundarios do polímero de almidón. Estas alternativas dan a posibilidade de estudar catro escenarios diferentes, dous de almidón hidrolizado e dous de forma oxidada.

Os perfís ambientais obtidos mostran unha importante implicación do recurso renovable, o almidón, nos bioadhesivos hidrolizados a base de almidón, sendo as categorías relacionadas coa acidificación, a ecotoxicidade e a toxicidade humana as nas que se observa un maior

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impacto, acadando valores que superan 70% no caso de categorías de impactos de toxicidade. As actividades de fondo asociadas á súa produción, cultivo, recolección e transporte son as principais razóns destas elevadas cargas. O motivo de tal variación en termos de efecto ambiental entre o tipo de activación do almidón é sinxela: cando o almidón se oxida, úsase menos deste recurso na formulación final do bioadhesivo, pero á súa vez, unha maior cantidade de outros produtos químicos. Este é o caso do almidón oxidado con bioadhesivo de sulfato ferroso, para o que o uso de acrilato de butilo ten unha carga ambiental que vai desde o 8% para a categoría de eutrofización mariña ata o 51% para as categorías de cambio climático e esgotamento de recursos, seguido do acetato de vinilo, con valores de impacto que van dende o 5% ata o 38%. Ademais, para a segunda alternativa de funcionalización de almidón oxidado, identificouse unha importante contribución do principal axente de reticulación utilizado na formulación, a resina de taninos.

Co obxectivo de seleccionar a mellor alternativa, tamén se desenvolve unha avaliación comparativa seguindo as metodoloxías de cálculo ReCipe MidPoint e EndPoint. Respecto ás alternativas de bioadhesivos a base de soia, a que acadou unha maior carga ambiental é o escenario proteína de soia formulada con anhídrido maleico en todas as categorías de impacto consideradas, a excepción das de cambio climático e esgotamento de ozono estratosférico. Pola contra, o escenario fariña de soia entrecruzada con dicianoamida considerouse como o máis adecuado, dadas as reducidas cargas ambientais en comparación co resto de alternativas. No que respecta aos escenarios baseados en almidón, a selección do mellor candidato é máis clara, xa que de forma media, a alternativa de oxidación con ferro a de menor carga ambiental en todas as categorías de impacto con só unha excepción, a categoría de saúde humana. Por outra banda, tamén se desenvolveu unha comparación EndPoint para a comparación tanto dos adhesivos de almidón, soia como as resinas sintéticas de uso común, coa que se puido observar que todas as puntuacións de dano obtidas son máis baixas para os bioadhesivos en comparación cos a base de formaldehido, sendo as alternativas con menor potencial de dano ambiental.

Capítulo 7. Novo enfoque ambiental baseado nunha combinación de límites planetarios e avaliación do ciclo de vida no mercado de bioadhesivos a base de madeira.

O obxectivo principal deste capítulo é ofrecer unha nova visión sobre a avaliación das cargas ambientais de novos escenarios de base biolóxica, como os dos adhesivos de base biolóxica para paneis de madeira. O principal inconveniente da metodoloxía ACV é que se centra principalmente nun momento e lugar determinados, baseándose nos datos do inventario do ciclo de vida, non obstante, para verificar cal é o potencial real de dano ambiental a maior escala, como un nivel planetario, requírese o uso dunha metodoloxía alternativa. Para iso, avalíanse os límites planetarios, considerando diferentes tipos de enfoques de asignación para ser conscientes do potencial sostible dos adhesivos de base biolóxica propostos tanto no **Capítulo 5** como no **Capítulo 6**. Respecto destas asignacións, considérase tanto os aspectos ambientais, económicos e sociais (é dicir, as emisións de gases de efecto invernadoiro (GEI) por país asociadas ao sector de paneis de madeira, o valor engadido bruto ou o gasto en consumo final, que tenta dar unha visión global sobre as demandas sociais, os gastos monetarios e a calidade de vida da comunidade). A metodoloxía requirida para ser aplicada iniciase coa aplicación da ACV, para obter as cargas de impacto ambiental asociadas por categoría de impacto e por tipo de composto. Cando se obteñen, aplícanse unha serie de factores de caracterización para transformar as puntuacións do ACV en puntuacións a nivel planetario, segundo os límites establecidos por tipo de categoría de impacto. Despois aplícanse os métodos de asignación para identificar a potencialidade dos escenarios desde diferentes perspectivas (é

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dicir, o punto de vista ambiental, económico e social), para comparalos entre eles e cos límites establecidos.

Por outra banda, cómpre mencionar que se propoñen tres escenarios principais: a nivel europeo, e a nivel nacional, seleccionáronse as rexións tanto de Suecia como de España. O motivo desta selección baseouse no feito de que Suecia, segundo a base de datos dispoñible, é a que presenta as puntuacións de valor engadido bruto máis altas de Europa e as emisións de GEI máis baixas, mentres que España ten un valor engadido bruto intermedio e un maior valor de emisións de GEI en comparación. Estas diferenzas nos valores son adecuadas para proporcionar un compendio de resultados de impacto e ratios de sustentabilidade ambiental, que proporciona unha visión integral e global dos graos potenciais de sustentabilidade de cada un dos factores de asignación considerados.

Os límites planetarios incluídos neste capítulo son aqueles para os que existe unha puntuación límite de impacto dispoñible en literatura, sendo aquelas as categorías de impacto do cambio climático, o esgotamento do ozono estratosférico, a acidificación dos océanos, os fluxos bioquímicos (nitróxeno e fósforo) e a carga de aerosois atmosféricos. Para calculalos, desenvolveuse un enfoque de arriba abaixo, unha redución de escala dos niveis planetarios aos niveis sectoriais e nacionais.

Unha das principais conclusións que se poden extraer deste enfoque de arriba cara abaixo é que o nivel de adecuación dos bioadhesivos e resinas sintéticas depende moito do tipo de asignación empregada, mentres que para as emisións de GEI e o gasto en consumo final todos os adhesivos están maioritariamente por debaixo dos valores límites, pola consideración do alcance do valor engadido bruto, algúns deles están fora dos límites, sendo este enfoque de asignación o máis prexudicado dende a perspectiva a nivel planetario.

A comparación entre as alternativas de adhesivos de madeira mostra a potencialidade dos adhesivos de base biolóxica, xa que na maioría dos casos están a ter un menor dano planetario en comparación co dos sintéticos, así como un índice de sustentabilidade axeitado. Non obstante, os resultados obtidos son diferentes segundo o tipo de asignación empregada, e tamén dependen do nivel sectorial, mentres que a rexión de España acada os peores valores en comparación co de Suecia, esperado dado o maior valor agregado bruto e os menores GEI desta última rexión.

***Sección IV**. Antimicrobianos*

O obxectivo principal desta sección é presentar escenarios alternativos de valorización para a produción de antimicrobianos, concretamente a nisina, un conservante natural con aplicacións recoñecidas na industria alimentaria, que axuden a substituír os conservantes químicos e os tratamentos térmicos que teñen un efecto negativo sobre as propiedades organolépticas e nutricionais dos produtos alimenticios. En particular, a produción biotecnolóxica de nisina desenvolvese utilizando fluxos de residuos industriais asociados aos alimentos (soro de queixo, polpa de remolacha e rastroxo de millo) (**Capítulo 8**) e residuos de base lignocelulósica (poda de oliveira e restos de eucalipto) (**Capítulo 9**).

O modelado do proceso a gran escala, o desenvolvemento dos balances de materia e enerxía, así como a valoración dos perfís ambientais e da viabilidade económica, son as principais aspectos realizados nos capítulos mencionados, co obxectivo de proporcionar unha análise exhaustiva e detallada dos escenarios de valorización de residuos propostos dende o punto de vista da sustentabilidade ambiental e económica.

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Capítulo 8. Produción biotecnolóxica de nisina a partir de residuos agroindustriais.

A utilización de diversos fluxos de residuos agroindustriais implica a necesidade de desenvolver diferentes etapas de pretratamento para a posterior fase de fermentación coa cepa *Lactococcus lactis*, necesaria para a produción de nisina, co-produtora tamén de ácido láctico. Tanto os residuos de polpa de remolacha azucreira (SBP) como os de rastroxo de millo (CS) requiren un intenso proceso de pretratamento, dada a necesidade de atacar á estrutura dos polisacáridos para permitir a liberación dos azucres fermentables. No caso da SBP foi necesaria unha acidificación a alta temperatura e unha hidrólise enzimática, mentres que para o CS foi necesaria unha autohidrólise e unha sacarificación enzimática. No caso do soro de queixo (CW), a fase de pretratamento é máis sinxela, dada a necesidade dun primeiro tratamento térmico e dunha segunda etapa de centrifugación, o que implica un beneficio no que respecta ao tempo de lote necesario, xa que os procesos encimáticos son máis esixentes de tempo, o que podería afectar sobre a capacidade de produción da instalación, de feito, mentres que para o SBP e CW os tempos de lote son similares, 77-79 h, para o caso do CS é significativamente superior, 144 h.

En canto á capacidade de produción de nisina, a alternativa de SBP é a que acada unha maior cantidade de nisina por proceso descontinuo, dada a súa maior dispoñibilidade de azucres fermentables para ser utilizados na fase de fermentación. Pola contra, o escenario menos prometedor é o de CS, non só polo maior tempo de lote, que reduce significativamente a súa viabilidade, senón tamén dadas as necesidades enerxéticas de todo o proceso.

Os perfís ambientais obtidos para as alternativas teñen unha certa analoxía ás principais conclusións acadadas sobre a capacidade tecnolóxica e de produción: a elevada carga ambiental da etapa de pretratamento nótase maioritariamente no escenario CS, sendo o uso das enzimas para o sacarificación enzimática as que supoñen un maior potencial de dano, pero tamén nas alternativas CW e SBP, neste caso dadas as necesidades de calor. En canto a materia prima, no caso do CS e SBP a contribución de impacto é insignificante, sen embargo percíbese unha achega máis significativa para o CW, cunha porcentaxe medio de carga ambiental que ascende a un 21,5%. Por outra banda, no que se refire á comparación baixo a perspectiva de danos potenciais, o escenario SBP é o que proporciona a menor carga ambiental, converténdoo así no escenario mellor prometedor. Mentres, pola contra, a alternativa CS é o escenario con maior impacto ambiental para a meirande de categorías analizadas.

Os resultados do estudo tecnoeconómico mostran que tanto os escenarios de valorización de CW como de SBP son economicamente rendibles, xa que se obtén un valor actual neto positivo, non obstante este non é o caso do CS, xa que o importe dos ingresos obtidos non son suficientes para compensar os custos anuais da instalación. Por outra banda, indo máis aló, tamén se presenta unha análise de ecoeficiencia tanto para as alternativas CW como SBP, ambas son viables economicamente, co fin de abarcar tanto os resultados ambientais como os económicos. As puntuacións obtidas para os tres índices de ecoeficiencia (beneficio neto/capacidade de produción/custos de produción fronte ás cargas ambientais) suxiren que o uso de SBP como recurso para a produción de nisina é a alternativa máis prometedora, xa que na maioría dos casos atópase en a rexión ecoeficiente, mentres que o CW atópase na non ecoeficiente nunha maior cantidade de categorías de impacto en comparación.

Por outra banda, aínda que o CS non acada rendibilidade económica, ao aplicar a metodoloxía *Greenness Grid*, que proporciona un valor de "índice verde" representativo do potencial de sustentabilidade, parece ter en consideración un escenario cun grao medio de potencialidade para ser considerado sostible, mentres que SBP segue a ser o que obtén a puntuación máis prometedora.

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Capítulo 9. Valorización de residuos agrícolas e forestais para a produción de nisina.

Neste capítulo lévase a cabo o deseño conceptual, a carga ambiental e a avaliación tecnoeconómica da produción biotecnolóxica de nisina mediante correntes secundarias non aproveitables agrícolas e forestais: podas de oliveira (OP) e residuos de eucalipto (ER). Como ocorreu no capítulo anterior tanto con SBP como con CS, é necesario realizar unha etapa de pretratamento para a liberación dos azucres fermentables dispoñibles na súa estrutura, baseada nunha etapa de autohidrólise, seguida dunha hidrólise enzimática para a fracción sólida e unha hidrólise ácida para a fracción líquida. Despois desenvólvese un proceso de fermentación utilizando a mesma cepa do capítulo anterior, *Lactococcus lactis*, seguido da recuperación de nisina cunha precipitación de sulfato de amonio e unha reacción de esterificación con metanol para a valorización do ácido láctico.

O modelado de procesos con SuperPro Designer demostra que o uso de OP proporciona unha maior cantidade de nisina e ácido láctico por proceso por lotes, mentres que necesita unha maior cantidade de tempo de lote, 163 h fronte ás 135 h da valorización ER. A razón destes resultados baséase no feito de que OP ten un menor contido en lignina, o que beneficia a liberación dos azucres fermentables na sección de pretratamento. O perfil ambiental que se obtén para ambas as alternativas revelou que o tramo de pretratamento é o de maior contribución para a maioría das categorías de impacto, para o caso do OP, e para todas elas no caso do escenario ER. A razón de tan importante impacto vén dada principalmente polas necesidades enerxéticas, sendo a electricidade máis perceptible que o vapor, con excepción da categoría de impacto da ecotoxicidade terrestre, para a que os requirimentos caloríficos implican máis da metade do impacto. No que respecta aos tramos de fermentación e augas abaixo, as necesidades enerxéticas seguen sendo as mais impactantes sobre as cargas ambientais do perfil obtido, pero para o de fermentación obsérvase certo impacto químico (principalmente o do K_2HPO_4), mentres que tamén as necesidades de HCl poderían ascender a un rango de impacto entre 3-18% nalgunhas categorías. Tendo en conta dar un escenario alternativo de impacto reducido, observouse que apostar polo uso de recursos renovables para as necesidades enerxéticas é a mellor estratexia de mellora ambiental.

Elabóranse tamén asignacións másicas e económicas para ambos os dous escenarios, para o que se observa que a asignación másica implica unha maior carga ambiental para a produción de ácido láctico, dado que a cantidade deste coproduto é significativamente maior en comparación coa cantidade de nisina producida, mentres que á hora de valorar a asignación económica, o alto prezo de venda da nisina en comparación co do ácido láctico dálle un beneficio á nisina pero, ao mesmo tempo, implica unha maior impacto sobre o potencial de dano ambiental.

Considerase tamén a comparación do potencial de dano das alternativas mediante a metodoloxía ReCiPe EndPoint, coa que se obtivo que o uso de OP é lixeiramente mellor que valorizar ER, pero as diferenzas non son tan significativas como para descartar o escenario de valorización do ER. Pero, no que respecta a adecuación económica, obtense que o valor actual neto do escenario OP é significativamente maior en comparación co de ER, en primeiro lugar pola maior cantidade de nisina e ácido láctico producidos ao ano, e en segundo lugar dados os custos directos e indirectos da planta, que son inferiores. Ademais, ao abarcar os resultados tanto ambientais como tecnoeconómicos, mediante o método da ecoeficiencia, observouse que, aínda que o escenario PO se sitúa sempre na rexión ecoeficiente, para os tres índices baixo estudo, o de ER non chega en ningún caso a esta rexión, sendo o escenario base (o non optimizado polo desenvolvemento da análise de sensibilidade) atopado sempre na rexión non

ecoeficiente. Ademais, as puntuacións obtidas polo desenvolvemento da metodoloxía *Greenness Grid* son análogas ás anteriores, sendo o OP o que acada o índice máis alto, sendo polo tanto máis potencial sostible. Pero aínda así, o escenario ER tamén acada un valor prometedor, por tanto, esta alternativa de valorización non se debería descartar como un escenario óptimo, tendo en conta que o seu potencial económico é menor en comparación co de OP.

Sección V. *Biopelículas activas*

Esta sección está centrada en abordar a produción biotecnolóxica dunha biopelícula activa con fins alimentarios mediante o uso da palla de trigo como recurso renovable, xunto co desenvolvemento dunha folla de ruta multicriterio para avaliar a idoneidade dun prototipo de biopelícula para uso alimentario. Neste sentido, o **Capítulo 10** trata a valorización da palla de trigo ao longo dun procedemento biotecnolóxico para a coprodución de nisina e ácido láctico e a posterior transformación do ácido láctico nunha biopelícula de PLA mediante o desenvolvemento de catro etapas principais de polimerización. Por outra banda, no **Capítulo 11** inclúese un modelo de estudo de películas de envases de base biolóxica no sector alimentario, tendo en conta tanto criterios técnicos, como a calidade ou capacidade de almacenamento dos envases, como os ambientais, sociais, criterios económicos e de circularidade.

Capítulo 10. Biopolímero PLA e nisina: unha biopelícula alimentaria activa.

Tanto o pretratamento, a fermentación como a etapa augas abaixo para a coprodución e recuperación de nisina e ácido láctico son análogos ao descrito no **Capítulo 9** da anterior ***Sección IV***. A principal novidade deste capítulo é, en primeiro lugar, a utilización dunha materia prima biolóxica alternativa, a palla de trigo, e, en segundo lugar, a valorización do ácido láctico coproducido na fermentación para a produción dunha película activa de base biolóxica, dada a adición da nisina producida no prototipo de biopelícula final, que serve como antimicrobiano con propiedades de conservación. A produción da película activa PLA tamén foi modelada na ferramenta SuperPro Designer, como unha etapa adicional do proceso, concretamente o subsistema catro, que require cinco pasos principais: oligomerización, prepolimerización, polimerización, purificación e produción final de película mediante un método de revestimento por difusión.

En canto á afectación de cada etapa do proceso ás cargas ambientais globais do proceso biotecnolóxico, observase que o potencial de dano é compartido entre os tramos augas abaixo e de pretratamento. A razón destes altos valores de impacto baséase principalmente nos requirimentos enerxéticos do proceso, sendo a electricidade a que presenta unha carga ambiental máis notable. Pola contra, a polimerización e produción de biopelículas é a etapa do proceso con menor carga ambiental asociada, o que dá un resultado positivo sobre a valorización do ácido láctico coproducido na fermentación.

O análise de sensibilidade en torno para os principais contribuíntes nas fases do proceso integrase para mostrar como as melloras que se poidan acadar para cada paso do proceso van afectar ao potencial de dano ambiental global do proceso. Tendo en conta isto, obtívose que os valores de redución que se poderían acadar están no intervalo do 27% ao 64%, obtendo así un media de redución do impacto ambiental que ascende a un 46%, un valor significativamente elevado que se adquire na súa maioría apostando polo uso de enerxías renovables e pola redución da dose de determinados produtos químicos empregados ao longo do proceso.

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Aplicase tamén neste capítulo unha metodoloxía adicional para acadar o grao de sustentabilidade da película PLA bioactiva, mediante o método *Greenness Grid*. Polo seu cálculo conclúese que o escenario podería ser catalogado como "potencialmente sostible" xa que alcanzou unha puntuación de 10,93. Por outra banda, buscando mellorar este valor, débese realizar maiores esforzos no que respecta á eficiencia enerxética do proceso e á capacidade de degradación de todos os compostos que forman parte do mesmo, que son os ítems nos que se acadaron puntuacións individuais máis baixas.

Capítulo 11. Mapa de decisións multicriterio para avaliar a sustentabilidade dos envases de alimentos.

Co obxectivo de proporcionar unha forma sinxela de estudar a adecuación dun produto/proceso en desenvolvemento a partir dun modelo prototipo, o **Capítulo 11** céntrase en propoñer un mapa multicriterio no que, a través do estudio e ponderación dos ítems que o integran, se poida concluír sobre á idoneidade dun produto ou proceso. Deste xeito, realízase unha primeira revisión bibliográfica dos aspectos fundamentais a ter en conta dende a primeira etapa do deseño, incluíndo tamén o grao de sustentabilidade e circularidade do prototipo, superando así a un modelo convencional, que baséase xenericamente en garantir simplemente a mínima calidade do produto e o cumprimento do obxectivo para o que foi creado.

Neste enfoque, o mapa multicriterio dividise en cinco etapas, a primeira referida ás características técnicas do prototipo de produto/proceso, seguida do estudo de criterios ambientais, entre as que destaca a avaliación da análise do ciclo de vida, unha terceira referida á medición da circularidade do proceso ou produto, na que se considera a reciclabilidade, a degradabilidade e o uso dos recursos, entre outros. Na cuarta etapa estúdase a viabilidade económica, sendo o valor actual neto e os parámetros de amortización os principais, aínda que nesta partida tamén se atopa a aplicación da metodoloxía de Custo do Ciclo de Vida e, finalmente, a quinta etapa sería a social, que se centra en identificar a aceptación do consumidor, o marketing desenvolvido, así como a imaxe do produto.

Unha vez construída a folla de ruta multicriterio, utilizouse para analizar o grao de idoneidade de dúas biopelículas alternativas de envasado de alimentos activos, unha delas adquirida de referencia bibliográfica (biopelícula de almidón, acetato de polivinilo e glicerol funcionalizada con nisina e nanocristais de celulosa) e a outro a do capítulo anterior (película de ácido poliláctico de palla de trigo activada con nisina). O desenvolvemento desta ruta multicriterio demostrou que hai algúns ítems que non se puideron cuantificar ou cualificar coa información dada pola modelización ou pola referencia bibliográfica, como por exemplo a capacidade de reciclabilidade ou a taxa de reutilización, pero o feito de que un material de base biolóxica se está producindo, que é biodegradable, que implica o aproveitamento de recursos residuais e que implica unha valorización dos recursos considérase suficiente para chegar á conclusión de que se cumpren os criterios de circularidade. Este foi o tipo de suposicións que se fixeron no estudo os escenarios anteriormente mencionados. Para concluír a discusión deste capítulo, só sinalar que ambos escenarios foron clasificados como "prototipos axeitados previstos", xa que cumpriron a maioría dos ítems incluídos en cada unha das fases do mapa multicriterio.

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Sección VI. *Antioxidantes*

Darlle un segundo alto valor engadido aos residuos procedentes do proceso produtivo agrícola e alimentario é o principal obxectivo desta **Sección VI**, na que se propoñen diversos esquemas de valorización para a recuperación de antioxidantes. Concretamente, no **Capítulo 12** propóñense diversas tecnoloxías de extracción, tanto convencionais como novas tecnoloxías emerxentes, para a valorización dos residuos da remolacha, tanto de follas como de talos, xa que está comprobado o seu alto contido en antioxidantes, favorecendo así a súa recuperación. Por outra banda, co obxectivo de proporcionar un modelo de biorefinería baixo un enfoque de economía circular, proponse o **Capítulo 13**, xa que se baseou no aproveitamento de residuos alimentarios e forestais, concretamente de diversas correntes relacionadas co viño (podas de vide procedentes das actividades de recolección e lías do viño, e mosto de uva do proceso de elaboración do viño), soro de queixo e residuos de eucalipto, para obter resveratrol, un antioxidante con propiedades moi recoñecidas para o seu uso nos sectores alimentario, farmacéutico e médico.

Capítulo 12. Estratexia biotecnolóxica para recuperar antioxidantes dos residuos de remolacha.

As tecnoloxías de extracción que se avalían neste capítulo foron tanto convencionais, incluíndo maceración (M) e extracción Soxhlet (S), como emerxentes, considerando ultrasóns (UAE), fluído supercrítico (SFE) e extracción líquida presurizada (PLE). A súa modelización a gran escala realizase en base á información dispoñible en bibliografía, incluíndose tamén a súa avaliación ambiental e tecnoeconómica, xunto coa comparación entre as tecnoloxías convencionais e as emerxentes sobre extraccións de antioxidantes. Ademais, como as correntes residuais son consideradas como materia prima, tamén se promove un enfoque circular. Os resultados do modelado de procesos demostran que o uso de tecnoloxías emerxentes realmente implica unha redución do tempo de lote do proceso de extracción, xa que mentres que para a extracción por ultrasóns o tempo necesario é de aproximadamente 11 h, para PLE 12,5 h e para SFE 15 h, cando se utiliza a extracción convencional os tempos de lote aumentan a 19 h para o Soxhlet e 106 h para a maceración, o que realmente implica unha redución da capacidade de produción da instalación.

Centrándose na cantidade de antioxidante que se podería obter por material de entrada, coa construción dos inventarios de ciclo de vida para a avaliación dos escenarios baixo a metodoloxía ACV, detectase que non existe unha analoxía sobre a eficacia da capacidade de extracción entre tecnoloxías convencionais e emerxentes. Mentres que para o procedemento de maceración é necesario unha cantidade de 0,64 kg de follas para obter 1 g de antioxidante, para o Soxhlet con 0,06 kg é suficiente, mentres que ao considerar a UAE, precísanse 0,29 kg, para PLE 0,09 kg e para SFE 0,07 kg. Pero, por outra banda, o que se viu é que a valorización das follas implica un maior beneficio en comparación co uso de talos, dada a súa maior composición en antioxidantes, que permite obter máis cantidade delas por material de entrada.

Os perfís ambientais das alternativas mostran que os requisitos enerxéticos son os que dan lugar a un maior potencial de dano ambiental na maior parte de todas as categorías de impacto nas tecnoloxías emerxentes, sendo a electricidade a máis significativa. No caso das tecnoloxías convencionais, para a de Soxhlet o uso do disolvente de extracción tamén é importante en case todas as categorías de impacto. Pola contra, para a alternativa de maceración o disolvente non ten un impacto tan significativo no perfil ambiental obtido, pero si o teñen requirimentos caloríficos cobra importancia, aínda máis que a da electricidade.

A análise tecnoeconómica establece que, efectivamente, a baixa capacidade de produción do método de extracción por maceración implica que o prezo mínimo de venda do antioxidante

obtido para garantir a rendibilidade económica da instalación ascende a 26 €/g para a valorización das follas e 81 €/g para os talos, que son sensiblemente superiores ao resto de alternativas, incluso coa de Soxhlet, para as que se obteñen 2,22 €/g e 4,80 €/g, respectivamente. No que respecta ás alternativas co prezo mínimo de venda esixido e, polo tanto, máis rendibles en termos económicos, son as de SFE e PLE. Con estas puntuacións a conclusión á que se pode chegar é que a mellora da capacidade de produción pola redución do tempo do lote implica realmente un beneficio desde o punto de vista económico, aínda que a cantidade de antioxidante obtida por proceso por lotes é inferior á dos métodos máis convencionais, como o de Soxhlet.

Ao comparar os escenarios baixo a metodoloxía EndPoint, conclúese que, cunha diferenza significativa, a extracción por ultrasonidos é o peor escenario, con cargas ambientais incrementadas, en comparación co resto de alternativas, que poderían alcanzar máis do 90% do diferenza. A razón destes resultados é dobre, en primeiro lugar pola reducida capacidade de produción e, en segundo lugar, polas altas necesidades enerxéticas. Por outra banda, ao comparar as tecnoloxías convencionais, é o escenario de Soxhlet o de menor potencial de dano ambiental pero, ao mesmo tempo, vagamente superior ao obtido para as tecnoloxías de extracción PLE e SFE. Ademais, coa realización da metodoloxía de ecoeficiencia, chégase á conclusión de que o escenario PLE é o mellor, tanto para a valorización de follas como de talos, adquirindo un índice de ecoeficiencia total para as catro categorías de impacto.

Capítulo 13. Valorización de residuos agroindustriais e forestais para producir resveratrol.

Neste capítulo realízase unha modelización a gran escala, 100 toneladas de residuos tratados por lote, da produción de resveratrol empregando residuos de viño, concretamente residuos da poda da vide, o mosto e as lías, soro de leite e residuos de eucalipto dentro fun enfoque de biorefinería. Tanto os residuos da poda como os de eucalipto requiren un pretratamento previo á fermentación para ser empregados como fonte de azucres fermentables, baseado nun proceso de autohidrólise a alta temperatura, seguido dunha post-hidrólise enzimática e/ou química, onde as unidades de polisacáridos se converten en unidades de monosacáridos. Pola contra, tanto os dous restantes residuos de viño como o soro de leite poden ser empregados de forma directa, aproveitándose previamente, no caso do soro de leite, o contido proteico, simplemente a través dunha serie de procesos de filtración.

Segundo os resultados de modelización obtidos, apreciase que a valorización dos residuos de poda de vide é a que proporciona maior cantidade de resveratrol por proceso por lotes, ascendendo a 0,28 toneladas/lote, mentres que para o mosto de uva este valor redúcese lixeiramente ate 0,24 toneladas/lote, para os residuos de eucalipto a 0.18 toneladas/lote e, as lías do viño e o soro de queixo só acadan 71 kg e 17 kg de resveratrol por proceso de lote, respectivamente.

Na avaliación tecnoeconómica observase a implicación deste pretratamento sobre os custos asociados das instalacións, xa que para os escenarios de mosto, lías e soro de queixo o custo dos equipamentos son significativamente menores. Por outra parte, no que respecta ao prezo mínimo de venta do resveratrol, é directamente proporcional á capacidade do proceso para a súa produción, así como o tempo requirido por lote, obténdose que os escenarios de soro de queixo e procesamento de lías son os que requiren un maior prezo de venta, mentres que o que emprega os residuos do mosto é que o adquire un menor valor.

O resultados ambientais evidencian que para tódalas alternativas os requirimentos enerxéticos son os que teñen un maior impacto sobre os perfís ambientais. Observouse certa contribución do medio de cultivo da etapa de fermentación, concretamente da dose de peptona, para as alternativas da valorización do mosto e das lías, mentres que este feito non se observou

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nos escenarios de valorización das podas, no que o etanol é o segundo elemento con maior impacto ambiental, nas mesmas categorías de impacto antes mencionadas. Neste sentido, propuxéronse escenarios de mellora de sensibilidade, nos que se observa que optar pola redución dos requirimentos enerxéticos e polo emprego de recursos renovables para a produción de enerxía son as accións correctoras máis adecuadas para diminuír o potencial dano.

Ademais, ao comparar os escenarios para a selección do máis axeitado dende a perspectiva ambiental, obtense que, para a maioría das categorías de impacto avaliadas, o uso do soro de queixo implica a maior dano sobre o medio ambiente, mentes que os escenario de mosto de uva é o máis prometedor, xa que se obteñen cargas ambientais reducidas e maiores ingresos. Non obstante, para reafirmar esta afirmación, e tamén para seleccionar a mellor segunda alternativa de valorización, tamén se desenvolve unha análise de ecoeficiencia. Os principais resultados subtraídos foron: (1) o escenario de valorización das lías non é unha alternativa ecoeficiente para ningún dos índices de ecoeficiencia, (2) tanto o mosto de uva como os residuos de poda de vide son substratos viables para a bioprodución de resveratrol.

Sección V. *Conclusións xerais*

Na última sección da tese inclúense as conclusións xerais obtidas a partires dos resultados obtidos en cada unha das seccións e capítulos que conforman o corpo da tese de doutoramento, así como una serie de recomendacións para a mellora, a futuro, dos escenarios de base biolóxica. Unha das principais conclusións que se poden obter desta tese é a necesidade de avaliar os novos procesos biolóxicos empregando metodoloxías baseadas nos eixes da sustentabilidade e da circularidade, para detectar os principais puntos fortes e febles, e así poder incrementar a súa potencialidade na cadea de mercado.

A falta de optimización dos novos procesos produtivos fronte os tradicionais baseados en recursos fósiles implica que, en ocasións, estes teñan un maior impacto ambiental en algunhas categorías de impacto, así como una menor viabilidade económica. Unha das principais razóns deste feito son os altos consumos de enerxía, que se detecta como un dos aspectos mais impactantes no perfil ambiental da meirande parte das alternativas de proceso estudadas. Si ben, a realización de análises de sensibilidade permitiu observar que tanto a optimización enerxética do proceso, pero sobre todo, optar por uso de enerxías renovables, implica una redución de impacto moi significativa, acadándose así factores de dano similares ou incluso menores que os procesos convencionais.

Por outra parte, ao longo desta tese, para determinar a sustentabilidade dos escenarios dende a perspectiva ambiental, utilizáronse diferentes metodoloxías, sendo a de ACV o foco central, pero tamén optando polo emprego dos principios de química verde, a través do método *Greenness Grid*, ou o análise de ecoeficiencia. Desta forma proporcionáronse diferentes enfoques, o que permite un maior coñecemento e unha análise mais profunda as alternativas de escenarios, incluíndose tamén o tecnoeconómico para a determinación da adecuación dos tipos de equipamento así como para identificar a viabilidade económica.

Polo tanto, esta tese de doutoramento propón unha serie de escenarios de base biolóxica co obxectivo de proporcionar novos modelos produtivos máis sostibles e que potencien o uso dos recursos de forma integral, promovendo así a economía circular da cadea de mercado. É importante destacar que o termo "bio" non sempre é sinónimo de "sustentable", xa que implica o desenvolvemento de procesos cun grao de optimización moito menor en comparación con modelos de produción máis convencionais baseados en recursos fósiles. Este feito quedou demostrado na maioría dos capítulos da tese, onde se comprobou que en diversos perfís ambientais, o consumo enerxético é o principal contribuínte aos impactos asociados, dada a falta de optimización enerxética e o baixo grao de desenvolvemento.

Por outra banda, cómpre mencionar que os procesos de valorización se desenvolveron mediante a modelización a gran escala utilizando datos de laboratorio, non a escala piloto, o que tamén implica que o grao de mellora e optimización é elevado, e polo tanto tamén os seus impactos asociados, así como como a súa viabilidade económica. Aínda que esta serie de inconvenientes pode reducir en certa medida a integración de procesos e produtos de base biolóxica no mercado, observouse que a maioría dos escenarios propostos ao longo desta tese son factibles dende o punto de vista económico, así como adecuados desde a perspectiva ambiental, tendo nalgúns casos un menor impacto asociado en comparación cos modelos de produción convencionais.

Desta forma, espérase que os resultados desta tese poderían considerarse como un paso máis na integración dos procesos produtivos de base biolóxica na cadea de mercado, que fomenten o aproveitamento integral dos recursos, a valorización de residuos e o uso de tecnoloxías máis respectuosas co medio ambiente.

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Abstract

The main objective of this doctoral thesis is the evaluation of the potential of biorefineries and biotechnological production schemes using waste streams from the perspectives of sustainability and circularity. To this end, various waste recovery strategies have been proposed, framed in the agro-industrial, forestry and food industry sectors, with the aim of obtaining a range of value-added products: bioadhesives for wood, antimicrobials, antioxidants and active biopackaging. The importance of this issue lies mainly in the fact that, at present, it is problematic to adequately manage the enormous amount of waste that is generated annually, which grows year after year, mainly due to the increase in population and the demand for goods and services. This fact implies important environmental impacts that can affect both the environment and human health, taking into account, for example, the emissions associated with a landfill management strategy (i.e. greenhouse effect gases, organic compounds, etc.). In addition, and perhaps equally important, is the fact that some of these residues could potentially be used as feedstock for biorefineries and biotechnological processes, given their content, for example, in antioxidants, fermentable sugars, or their physicochemical properties. To do this, the scenarios offered in this thesis can help address these problems and choose the most appropriate waste management and recovery strategies in terms of sustainability and circular economy.

In ***Section I*** and ***Section II***, an introduction to the main issues related to the recovery of waste streams is described and discussed, together with its main environmental and management constraints. On the other hand, it is also in this section of the thesis where the main methodologies used for the analysis of the scenarios are described: the Life Cycle Assessment (LCA) as the relationship between all the chapters and sections, with the objective of analyzing of the environmental loads and profiles of the scenarios, techno-economic evaluation, to analyze the economic viability of the proposed recovery alternatives, and eco-efficiency analysis, to study the interrelationship between the economic and environmental perspectives in order to select the best scenarios.

Section III. *Formaldehyde-free Bioadhesives for Wood-based Panels*

This section offers alternative formaldehyde-free adhesives for the wood-based panel sector using lignocellulosic, tannin-based and agri-food waste streams. Specifically, the waste streams that are valued are: Kraft Lignin, coming from the Kraft pulp process, Organosolv Lignin, obtained from Organosolv pulp, Tannins (**Chapter 5**), obtained mainly from the debarking and processing of wood, Soybean, as a residue from the transformation of the soybean crop for further production, and starch (**Chapter 6**), obtained from the valorization of corn residues.

In order to have all the necessary data to carry out the LCA methodology, a large-scale production model of bioadhesives was carried out, taking into account the production capacity of synthetics, in order to provide a comparison at an analogous production level. In addition to the LCA, an impact assessment was conducted at the planetary boundary level, a further step in assessing the strength of a particular bio-based scenario from an environmental point of view. This approach, which is developed in **Chapter 7**, provides a more global view of the potential of biobased, taking into account the damage limits set by the thresholds.

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Chapter 5. Bioadhesives derived from lignocellulosic waste streams, forestry and paper industry.

The use of lignin as a resource to produce bioadhesives requires a functionalization/activation step to favor the reaction with the crosslinkers necessary for the final adhesive formulation. This activation step can be carried out by different methods, among which glyoxalation is one of the most widely used in the literature. However, it has been observed that this functionalization step using glyoxal as activating agent is very harmful to the environment, mainly due to the amount of energy required for this step of the process, which is the main critical point identified. In fact, the electrical contribution to the environmental profile of this first stage is higher than 80% for mainly all the impact categories. This results in an environmental contribution of lignin in the bioadhesive formulation profile above 60% for most of the environmental impact categories. This fact leads, to some extent, to a reduction of the potential of lignin as a renewable resource for bioadhesive production.

Given the high impact of glyoxalation, an alternative functionalization process, al alternative agent has been used, dimethyl carbonate (DMC), thus providing an isocyanate-free polyurethane-lignin bioadhesive with reduced environmental loads compared to glyoxal activation. This improvement effect was demonstrated from the impact values obtained after the development of the LCA methodology. Specifically, in three impact categories a more noticeable reduction: global warming potential, terrestrial ecotoxicity and fossil resource scarcity.

In order to offer alternative scenarios for bioadhesives, with the aim of trying to improve their environmental perspective, a sensitivity analysis was carried out on the process variables that contributed most to the environmental profile. It was observed that the reduction of energy demand, as well as the commitment to the use of renewable energies, are the options with which a more noticeable improvement in the environmental loads obtained is achieved. On the other hand, another conclusion reached is that the impact of the chemicals used in the formulation is not so high, except in the case of hexamethylenediamine, where an important contribution is observed in the environmental profile.

Tannins from condensed bark chips has also been used, thus providing five bioadhesive scenarios, differentiated mainly by the type of crosslinking agent used for the final bioadhesive formulation. The process implies the need to develop two main stages: the production of the condensed tannin and the crosslinking with the appropriate chemical agent. Compared to what happened with lignin activation, the tannin condensation stage to favor its functionalization is not so impacting, in fact, its environmental contribution on the obtained profiles does not exceed 20-30%, which favors the potential of this biological resource in the formulation of wood adhesives. This fact is demonstrated by the application of the LCA methodology, which shows that, indeed, the environmental loads obtained for tannin-based bioadhesives are significantly lower than those of lignin, with the exception of the non-isocyanate polyurethane Organosolv bioadhesive alternative, which have similar scores.

The sensitivity scenarios for tannin-based bioadhesives are based on both reduced energy requirements and reduced chemical dosage, since in these cases, some chemical agents certainly have a significant contribution to the profile. The scores obtained showed that the use of ethyl carbonate instead of dimethyl carbonate really implies a significant benefit, reaching impact reduction values that could reach more than 80% in categories such as acidification and eutrophication, while the reduction of electrical requirements provides an improvement. scenarios in a 20% reduction in most of the impact categories.

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Regarding the best alternative for tannin bioadhesives, according to the scores obtained by the development of the LCA methodology, it is observed that the use of hexamethylenediamine as a crosslinking agent is the one that achieves lower environmental loads in almost all impacts. categories, with the exception of global warming, ecotoxicity and scarcity of fossil resources, given the electricity and steam requirements, which are higher than the rest of the scenarios. However, when analyzing the alternatives using the ReCiPe EndPoint method, it was found that not only the bioadhesive mentioned, but all of them achieved a damage potential and single score value lower than those of the PF synthetic resin and, in the case of tannins crosslinked with paraformaldehyde, glyoxal and hexamine, lower also compared to urea formaldehyde and melamine urea formaldehyde resins, the most widely used in the wood-based panel industry.

Chapter 6. Bioadhesives obtained from food industry waste.

Looking for the use of soybean as raw material for the production of bioadhesives, two main alternatives has been developed, the direct use of soybean meal or the development of a pretreatment stage for the acquisition of soy protein, with improved adhesion quality and mechanical properties, both of which are subsequently crosslinked with the appropriate chemical agents, with the objective of achieving adhesion characteristics similar to those of common synthetic resins (i.e., structural quality of the board, moisture tolerance, etc.).

The improved adhesion properties achieved by protein extraction for soybean meal also provide beneficial results given their contribution to the environmental profile, which is similar, or in some cases, slightly lower than the use of soybean meal for some of the impacts categories, with the exception of the marine eutrophication impact category, since no matter whether soybean meal or soy protein is used, the impact is similar.

As for the main contributors to the environmental profiles obtained, with the exception of the soy protein alternative cross-linked with tannin resin, where electricity is the main hot spot, the main environmental contributors are the cross-linking agents used for the formulation of the bioadhesives, reaching maximum influence values of 60% to 90% for the soybean meal alternatives, and 50% to 70% for the soy protein alternatives. The impact categories most affected by this are those related to acidification, eutrophication and human health.

Another alternative under study is starch, which requires a pre-treatment stage for its functionalization, as happened with the lignin resource, the direct use is not effective to be used for the formulation of bioadhesives. With this first activation stage, a greater number of active centers are formed, which implies a higher yield in the crosslinking stage, and a reduction in viscosity is achieved, resulting in better adhesive mechanical properties. For this purpose, two main pretreatment alternatives were evaluated: starch hydrolysis and oxidation of the primary and secondary hydroxyl groups of the starch polymer. These alternatives give the possibility to provide four different scenarios, two of hydrolyzed starch and two of oxidized form.

The environmental profiles obtained show a significant contribution of the renewable resource starch in starch-based hydrolyzed bioadhesives, with the categories related to acidification, ecotoxicity and human toxicity showing the greatest impact, with contribution values exceeding 70% in the case of toxicities related to human health. The background activities associated with their production, cultivation, harvesting and transport are the main reasons for these high loads. The reason for such variation in terms of environmental effect between the type of starch activation is simple: when starch is oxidized, less of this resource is used in the final formulation of the bioadhesive, but in turn, a greater amount of other chemicals. This is the case for the starch bioadhesive oxidized with ferrous sulphate, for which the use of

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butyl acrylate has an environmental contribution ranging from 8% for the marine eutrophication category to 51% for the climate change and resource depletion categories, followed by vinyl acetate, with impact values ranging from 5% to 38%. In addition, for the second oxidized starch functionalization alternative, a significant contribution of the main crosslinking agent used in the formulation, tannin resin, was identified.

In order to select the best alternative, a comparison was developed following the ReCipe MidPoint and EndPoint calculation methodologies. Regarding the soy-based bioadhesive alternatives, the one with the highest environmental burden is the soy protein scenario formulated with maleic anhydride, with the exception of climate change and stratospheric ozone depletion. In contrast, the dicyanoamide cross-linked soybean meal scenario was considered the most attractive, given the lower environmental burdens compared to the rest of the alternatives. As for the starch-based scenarios, the selection of the best candidate is clearer, since, on average, the iron oxidation alternative has the lowest environmental burden in all impact categories with only one exception, the human health category.

On the other hand, an EndPoint comparison was also developed between starch, soy and commonly used synthetic resins, which showed that all the damage scores obtained are lower for bioadhesives compared to those based on formaldehyde, being the alternatives with the lowest potential for environmental damage similar to those obtained by the MidPoint methodology.

Chapter 7. New environmental approach based on a combination of planetary boundaries and life cycle assessment in the wood-based bioadhesives market.

The main objective of this chapter is to provide a new perspective on the assessment of environmental burdens of new bio-based scenarios, such as those of bio-based wood panel adhesives. The main drawback of the LCA methodology is that it focuses primarily on a particular time and place, based on life cycle inventory data; however, to verify what the actual potential for environmental damage is on a larger scale, such as at the planetary level, the use of an alternative methodology is required. For this, planetary boundaries are studied, considering different types of allocation approaches to know the sustainable potential of bio-based adhesives proposed in both **Chapter 5** and **Chapter 6**. As for these allocations, they are based on environmental criteria, economic and social aspects (i.e. greenhouse gas (GHG) emissions per country associated with the wood-based panel sector, gross value added or final consumption expenditure, which tries to give a global view of the social demands, monetary expenditure and quality of life of the community). The required methodology to be applied starts with the application of the LCA, to obtain the associated environmental impact loads by impact category and by type of composite. When obtained, a series of characterization factors are applied to transform the LCA scores into planetary level scores, according to the thresholds established by type of impact category. Allocation methods are then applied to assess the suitability of the scenarios from different perspectives (i.e., environmental, economic and social), to compare them with each other and with the thresholds set by impact category.

On the other hand, it is worth mentioning that three main scenarios were considered: at the European level, and at the national level, the regions of both Sweden and Spain were selected. The reason for this selection was based on the fact that Sweden, according to the available database, has the highest gross value-added scores in Europe and the lowest GHG emissions, while Spain has intermediate gross value added and higher GHG emissions. emissions in comparison. These differences in values are adequate to provide a compendium of impact

scores and environmental sustainability ratios, which provides a complete and comprehensive view of the possible degrees of sustainability of each of the allocation factors considered.

The planetary boundaries assessed in this chapter are those for which there is an impact threshold score available in the literature, these being the impact categories of climate change, stratospheric ozone depletion, ocean acidification, biochemical fluxes (nitrogen and phosphorus) and atmospheric aerosol loading. To calculate these, a top-down approach was developed, a downscaling from planetary to sectoral and national levels.

One of the main conclusions that can be drawn from this top-down approach is that the level of adequacy of the alternative bioadhesives and synthetic resins is highly dependent on the type of allocation used, while for GHG emissions and final consumption expenditure, all adhesives are mostly below. the threshold values, due to the consideration of the scope of gross value added, some of them are going out of bounds, this allocation approach being the most damaged from the planetary level perspective.

The comparison between wood adhesive alternatives shows the potential of bio-based adhesives, as in most cases they are having less planetary damage compared to synthetics, as well as an adequate sustainability index. However, the results obtained are different according to the type of allocation used, and also depend on the sectoral level assessed, while the region of Spain reaches the worst values compared to Sweden, expected given the higher gross value added and lower GHG of the latter region.

Sección IV. *Antimicrobials*

The main objective of this section is to present alternative valorization scenarios for the production of antimicrobials, specifically nisin, a natural preservative with recognized applications in the food industry, which help to replace chemical preservatives and thermal treatments that have a negative effect on the organoleptic and nutritional properties of food products. In particular, the biotechnological production of nisin is developed from food-associated industrial waste streams (cheese whey, beet pulp and corn stover) (**Chapter 8**) and lignocellulosic-based waste (olive pruning and eucalyptus residues) (**Chapter 9**).

The modelling of the large-scale process, the development of mass and energy balances, as well as the provision of the environmental profiles and the economic feasibility, are the main aspects assessed in the aforementioned chapters, with the aim of providing a comprehensive vision and detailed analysis for the demonstration of the feasibility of the proposed waste valorization scenarios from the point of view of environmental and economic sustainability.

Chapter 8. Biotechnological production of nisin from agroindustrial wastes.

The use of various agro-industrial waste streams implies the need to develop different pretreatment stages for the subsequent fermentation phase with the Lactococcus lactis strain, necessary for the production of nisin, which also co-produces lactic acid. Both sugar beet pulp (SBP) and corn stover (CS) residues require an intensive pretreatment process, given the need to cleave the polysaccharide structure to allow the release of fermentable sugars. In the case of SBP, high temperature acidification and enzymatic hydrolysis were required, while autohydrolysis and enzymatic saccharification were required for CS. In the case of cheese whey (CW), the pretreatment phase is simpler, given the need for a first heat treatment and a second centrifugation step, which implies a benefit in terms of the batch time required, since the enzymatic processes are more time demanding, which could affect the production capacity of

the facility, in fact, while for SBP and CW the batch times are similar, 77 and 79 h respectively, for the case of CS it is significantly higher, 144 h.

In terms of nisin production capacity, the SBP alternative achieves the highest amount of nisin per batch process, given its higher availability of fermentable sugars to be used in the fermentation phase. On the contrary, the least promising scenario is that of CS, not only because of the longer batch time, which significantly reduces its feasibility, but also because of the energy requirements of the whole process.

The environmental profiles obtained for the alternatives give some analogy with the main conclusions reached in the assessment of technological and productive capacity: the high environmental contribution of the pretreatment stage is mostly noted in the CS scenario, with the use of enzymes for enzymatic saccharification presenting the greatest potential for damage, but also in the CW and SBP alternatives, in this case given the heat requirements. Regarding the source, while for CS the impact contribution is negligible, and for SBP almost negligible for most of the impact categories, the contribution of CW is more significant, with a percentage of environmental load. between 4% for the fossil resource scarcity impact category and 70% for SOD, with an average contribution value of 21.5%. On the other hand, when it comes to the comparison under the perspective of potential damages, the SBP scenario is the one with the lowest environmental load, making it the most promising scenario. Meanwhile, on the contrary, the CS alternative represents the highest environmental contribution for most of the impact categories subject to study.

The results of the techno-economic assessment showed that both the CW and SBP valuation scenarios are economically profitable, since a positive net present value is obtained, however this is not so for the CS, since the amount of revenue obtained is not sufficient to offset the annual costs of the facility. On the other hand, going further, an eco-efficiency analysis was also developed for both the CW and SBP alternatives, both economically viable, in order to cover both environmental and economic results. The scores obtained for the three indices (net benefit/production capacity/production costs versus environmental burdens) suggest that the use of SBP as a resource for nisin production is the most promising alternative, as it is in the most environmentally. efficient region, while CW is in the non-eco-efficient in a larger number of impact categories in comparison.

On the other hand, while CS does not achieve economic profitability when evaluating the techno-economic assessment, when applying the Greenness Grid methodology, which provides a "green index" value representative of sustainability potential, it appears to take into consideration a scenario with a medium-grade potential to be considered sustainable, while SBP remains the most promising score.

Chapter 9. Valorization of agricultural and forestry residues for nisin production.

This chapter provides the conceptual design, environmental load and techno-economic analysis of the biotechnological production of nisin from unusable agricultural and forestry by-products: olive pruning (OP) and eucalyptus residues (ER). As happened in the previous chapter with both SBP and CS, a pretreatment step is necessary to release the available fermentable sugars in their structure, based on an autohydrolysis step, followed by an enzymatic hydrolysis for the solid fraction and a post-hydrolysis acid hydrolysis for liquid fraction. A fermentation process is then developed using the same strain as in the previous chapter, *Lactococcus lactis*, followed by a subsequent process based on nisin recovery with ammonium sulphate precipitation and an esterification reaction with methanol for lactic acid valorization.

Process modellingwith SuperPro Designer shows that the use of OP provides a higher amount of nisin and lactic acid per batch process, while requiring a higher amount of batch time, 163 h compared to 135 h for ER valorization. The reason for these results is based on OP having a lower lignin content, which benefits the release of fermentable sugars in the pretreatment section, thus providing a greater carbon source for the fermentation process and subsequently producing more nisin.

The environmental profile obtained for both alternatives revealed that the pretreatment section is the largest contributor for most of the impact categories under evaluation, in the case of the OP, and for all of them for the case of the ER scenario. The reason for such an important impact is mainly given by the energy requirements, with electricity being more noticeable than steam, with the exception of the terrestrial ecotoxicity impact category, where the calorific requirements account for more than half of the impact. As for the fermentation and downstream sections, energy requirements remain one of the main contributors to the environmental loads of the obtained profile, but for the fermentation section some chemical impact (mainly K_2HPO_4) is observed, while for the downstream also HCl requirements could increase to a range of 3-18% of the contribution in some categories. Considering an alternative scenario of reduced impact, it was observed that opting for the use of renewable resources for energy needs is the best environmental improvement strategy.

Mass and economic allocations are also elaborated for both scenarios, for which it is observed that the mass allocation implies a higher environmental contribution for the production of lactic acid, since the amount of this co-product is significantly higher with respect to the amount of lactic acid. nisin produced by batch process, while when considering the economic allocation, the high selling price of nisin compared to lactic acid gives a benefit to nisin but, at the same time, implies a higher contribution on the potential for environmental damage.

A comparison of the damage potential of the alternatives was also considered using the ReCiPe EndPoint methodology, with which it was obtained that the use of OP is slightly better than the ER valuation, but the differences are not so significant as to discard the ER valuation scenario. But, when evaluating the economics, it is seen that the net present value obtained by the OP scenario is significantly higher compared to the ER scenario, firstly because of the higher amount of nisin and lactic acid produced per year, and secondly given the total direct costs and indirect costs of the plant, which are lower. Furthermore, when covering both the environmental and techno-economic results, using the eco-efficiency method, it was observed that, although the OP scenario is always located in the eco-efficient region, for the three indexes, the ER scenario does not reach this region in any case, with the base scenario (the one not optimized by the development of the sensitivity analysis) always being in the non-eco-efficient region. In addition, the scores obtained by the development of the Greenness Grid methodology are similar to the previous ones, with the PO achieving the highest index, so it has a more sustainable potential. But even so, the ER scenario also achieves a value under this categorization, which is why it was previously indicated that, given the similarity in the results obtained, this valuation alternative could not be discarded, considering that its economic potential is lower compared to the OP.

Section V. *Active biofilms*

This section focuses on addressing the biotechnological production of an active biofilm for food purposes using wheat straw as a renewable resource, together with the development of a multi-criteria roadmap to assess the adequacy of a biofilm prototype for food applications. In

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this sense, **Chapter 10** deals with the valorization of wheat straw along a biotechnological procedure for the co-production of nisin and lactic acid and the subsequent transformation of lactic acid into a PLA biofilm through the development of four main polymerization steps. On the other hand, **Chapter 11** includes a model for the evaluation of bio-based packaging films in the food sector, taking into account both technical issues, such as the quality or storage capacity of the packaging, and environmental, social, economic and circularity criteria.

Chapter 10. PLA biopolymer and nisin: an active food biofilm.

The pretreatment, fermentation and downstream sections for the co-production and recovery of nisin and lactic acid are analogous to those described in **Chapter 9** of **Section IV** above. The main novelty of this chapter is, firstly, the use of an alternative biological feedstock, wheat straw, and secondly, the valorization of the lactic acid co-produced in the fermentation for the production of an active biofilm, given the addition of the nisin produced in the final biofilm prototype, which serves as an antimicrobial with preservative properties. The production of active PLA film was also modelled in the SuperPro Designer tool as an additional stage of the process, specifically subsystem four, which requires five main steps: oligomerization, prepolymerization, polymerization, purification and final film production using a diffusion coating method.

In terms of the contribution of each process step to the overall environmental burdens of the biotechnological process, it is observed that the potential for damage is shared between the downstream and pretreatment steps. The reason for these high contributions is mainly based on the energy requirements of the process, with electricity having the highest environmental load. In contrast, polymerization and biofilm production is the process step with the lowest associated environmental load, which gives a positive result in the valorization of lactic acid co-produced in fermentation.

The environmental sensitivity assessment for the main contributors in the process steps is integrated to show how improvements that can be achieved for each process step will affect the overall environmental damage potential of the process. Taking this into account, it was obtained that the reduction values that could be achieved are in the range of 27% to 64%, thus obtaining an average reduction of the environmental impact amounting to 46%, a significantly high value that is acquired mostly by opting for the use of renewable energies and by reducing the dosage of certain chemicals used throughout the process.

This chapter also applies an additional methodology to evaluate the degree of sustainability of the bioactive PLA film, using the Greenness Grid method, based on the principles of Green Chemistry, thus covering environmental aspects as well as the safety and efficiency of the process. By its calculation it is concluded that the scenario could be categorized as "potentially sustainable" as it reached a score of 10.93. On the other hand, seeking to improve this value, greater efforts should be made within the energy efficiency of the process and the degradation capacity of all the compounds that are part of it, which are the items in which the lowest individual scores were achieved.

Chapter 11. Multi-criteria decision map for assessing the sustainability of food packaging.

With the aim of providing a simple way to evaluate a product/process under development from a prototype model, **Chapter 11** focuses on proposing a multi-criteria map in which, through the scoring and weighting of the items that compose it, can be concluded. The results

can be achieved in terms of the suitability of a product or process. In this way, a first bibliographic review of the fundamental aspects to be considered from the first stage of the design is carried out, including also the study of the degree of sustainability and circularity of the prototype, thus overcoming a conventional model, which is generally based on the simple guarantee of the minimum quality of the product and the fulfillment of the objective for which it was created.

In this approach, the multi-criteria map is divided into five stages, the first one referring to the technical characteristics of the product/process prototype, followed by an evaluation of environmental criteria, among which the life cycle analysis stands out, a third one referring to the measurement of the circularity of the process or product, in which the recyclability, degradability and use of resources, among others, are assessed. In the fourth stage, the economic viability is studied, being the net present value and the amortization parameters the main ones, although this section also includes the application of the Life Cycle Cost methodology and, finally, the fifth stage would be the social one, which focuses on identifying consumer acceptance, the marketing developed, as well as the image of the product.

Once the multi-criteria roadmap was constructed, it was used to analyze the degree of suitability of two alternative biofilms for active food packaging, one of them acquired from a bibliographic reference (biofilm of starch, polyvinyl acetate and glycerol functionalized with nisin and cellulose nanocrystals) and the other from the previous chapter (nisin-activated wheat straw polylactic acid film). The development of this evaluation showed that there are some items that cannot be scored with the information given by modelling or literature reference, such as recyclability or reusability rate, but the fact that a bio-based material is being produced, that it is biodegradable, that it involves the use of waste resources and that it enables resource valorization is considered sufficient to conclude that the "circularity criteria" are met, for example. This was the type of assumption made in studying the scenarios mentioned above. To conclude the discussion of this chapter, just note that both scenarios analyzed under the new metrics were classified as "expected adequate prototypes" as they met most of the elements included in each of the multicriteria roadmap phases.

Section VI. *Antioxidants*

Giving a second high added value to waste from the agri-food production process is the main objective of this Section VI, in which various valorization schemes for the recovery of antioxidants are proposed. Specifically, **Chapter 12** proposes various extraction technologies, both conventional and newly emerging, for the valorization of beet wastes, both leaves and stalks, since their high antioxidant content has been demonstrated, thus favouring their valorization. On the other hand, with the objective of providing a biorefinery model under a circular economy approach, **Chapter 13** is proposed, as it was based on the utilization of food and forestry wastes, specifically from various streams related to wine (vine pruning, wine lees and grape must), cheese whey and eucalyptus residues, to obtain resveratrol, an antioxidant with known properties for use in the food, pharmaceutical and medical sectors.

Chapter 12. Biotechnological strategy to recover antioxidants from beet residues.

The extraction technologies being considered in this chapter were both conventional, including maceration (M) and Soxhlet extraction (S), and emerging, considering ultrasound (UAE), supercritical fluid (SFE) and pressurized liquid extraction (PLE). Their large-scale modelling is performed based on the information available in the literature, including also their

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environmental and techno-economic assessment, together with the comparison between conventional and emerging technologies on antioxidant extractions. In addition, since waste streams are considered as feedstock, a circular approach was also evaluated. The process modelling results show that the use of emerging technologies actually implies a reduction in the batch time of the extraction process, since while for UAE the time required is approximately 11 h, for PLE 12.5 h and for SFE 15 h, when conventional extraction is used the batch times increase to 19 h for Soxhlet and 106 h for maceration, which actually implies a reduction in the production capacity of the facility.

Focusing on the amount of antioxidant that could be obtained per input material, with the construction of the life cycle inventories for the assessment of the scenarios under the LCA methodology, it was detected that there is no analogy on the effectiveness of the extraction capacity between conventional and emerging technologies. While for the maceration procedure a quantity of 0.64 kg of leaves is needed to obtain 1 g of antioxidant, for Soxhlet 0.06 kg is sufficient, considering UAE 0.29 kg is needed, for PLE 0.09 kg and for SFE 0.07 kg. But, on the other hand, what has been seen is that the valorization of leaves implies a greater benefit compared to the use of stems, given their greater composition in antioxidants, which makes it possible to obtain more of them per raw material.

The environmental profiles of the alternatives show that energy requirements are the main contributors to the potential for environmental damage in most impact categories when assessing emerging technologies, with electricity being the most significant. In the case of conventional technologies, for Soxhlet the use of extraction solvent is also significant in almost all impact categories. On the contrary, for the maceration alternative, the solvent does not have such a significant impact on the environmental profile obtained, but the contribution of the calorific requirements becomes important, even more than that of electricity.

The technical-economic evaluation establishes that, indeed, the low production capacity of the extraction method by maceration means that the minimum selling price of the antioxidant obtained to ensure the economic profitability of the facility is 26 €/g for the recovery of leaves and 81 €/g for stems, which are significantly higher than the other alternatives, including Soxhlet, for which 2.22 €/g and 4.80 €/g, respectively, are obtained. As for the alternatives with the minimum required selling price and, therefore, more profitable in economic terms, they are SFE and PLE. With these scores, the conclusion that can be drawn is that the improvement in production capacity due to the reduction in batch time is indeed a benefit from an economic point of view, although the amount of antioxidant obtained per batch process is lower than that of more conventional methods, such as Soxhlet.

When comparing the scenarios under the EndPoint methodology, it is concluded that, with a significant difference, ultrasonic extraction is the worst scenario, with higher environmental burdens, compared to the rest of the alternatives, which could reach more than 90% of the difference. The reason for these results is twofold, firstly because of the reduced production capacity and secondly because of the high energy requirements. On the other hand, when comparing the conventional technologies, the Soxhlet scenario has the lowest potential for environmental damage but, at the same time, slightly higher than that obtained for the PLE and SFE extraction technologies. On the other hand, the eco-efficiency methodology concludes that the PLE scenario is the best, both for the recovery of leaves and stems, acquiring a total eco-efficiency index for the four impact categories when evaluating the recovery of leaves.

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Chapter 13. Valorization of agro-industrial and forestry wastes to produce resveratrol.

This chapter performs a large-scale modelling, 100 tons of waste treated per batch, of the production of resveratrol from wine residues, specifically vine pruning residues, must and lees, whey and eucalyptus residues in a fun biorefinery approach. Both pruning residues and eucalyptus residues require a pretreatment prior to fermentation to be used as a source of fermentable sugars, based on a high temperature auto-hydrolysis process, followed by an enzymatic and/or chemical post-hydrolysis, where polysaccharide units are converted into monosaccharide units. On the contrary, both the two remaining wine pomaces and the whey can be used directly, taking advantage of the protein content in the case of whey, simply by a series of filtration processes.

According to the modelling results obtained, it can be observed that the valorization of vine pruning residues is the one that contributes the highest amount of resveratrol per batch process, amounting to 0.28 ton/batch, while for grape must this value is slightly reduced to 0.24 ton/batch, for eucalyptus residues to 0.18 ton/batch, and wine lees and cheese whey only reach 71 kg and 17 kg of resveratrol per process batch, respectively.

The technical-economic study shows the implication of this pretreatment on the associated costs of the facilities, since for the must, lees and cheese whey scenarios the cost of the equipment are significantly lower in comparison. On the other hand, as for the minimum selling price of resveratrol, it is directly proportional to the capacity of the process for its production, as well as the time required per batch, making the whey and cheese lees processing scenarios the indicated ones. which require a higher selling price, while the one that takes advantage of the must waste acquires a lower value.

The environmental assessment shows that, for all alternatives, the energy requirements contribute the most to the environmental profiles. Some contribution from the fermentation stage culture medium, specifically peptone dosage, was observed for the must and lees valorization alternatives, while this fact was not observed in the pruning valorization scenarios. scenario, where ethanol is the second largest contributor, in the same impact categories mentioned above. In this sense, sensitivity improvement scenarios were proposed, in which it is observed that opting for the reduction of energy requirements and the use of renewable resources for energy production are the most appropriate corrective actions to reduce potential damage.

Furthermore, when comparing the scenarios for the selection of the most suitable from an environmental perspective, it is obtained that, for most of the impact categories evaluated, the use of cheese whey implies the greatest environmental contribution, with the exception of environmental impact. categories, that the grape must scenario is the most promising since lower environmental burdens and higher revenues are obtained. However, to reaffirm this statement, and to select the second-best valorization alternative, an eco-efficiency analysis is also developed. To this end, the main outcomes were: (1) the lees valorization scenario is not an eco-efficient alternative for any of the evaluated indexes, (2) both grape must and vine pruning remains are viable substrates for resveratrol bioproduction.

***Section V**. General conclusions*

The last section of the thesis includes the general conclusions obtained from the results obtained in each of the sections and chapters that make up the body of the doctoral thesis, as well as a series of recommendations for the improvement, in the future, of the biobased proposed production alternatives. One of the main conclusions that can be drawn from this

thesis is the need to evaluate new biological processes using methodologies based on the axes of sustainability and circularity, in order to detect the main strengths and weaknesses, and thus be able to increase their potential in the market chain.

The lack of optimization of the new production processes compared to the traditional ones based on fossil resources implies that, on occasions, these have a greater environmental impact in some impact categories, as well as a lower economic viability. One of the main reasons for this fact is the high energy consumption, which is detected as one of the major contributors to the environmental profile of most of the process alternatives studied. However, the performance of sensitivity analysis allowed to observe that both the energy optimization of the process, but above all, opting for the use of renewable energies implies a very significant impact reduction, thus achieving similar or even lower damage factors than conventional processes.

Besides, throughout this thesis, for the evaluation of this environmental perspective, different methodologies were used, being the LCA the central axis, but also opting for the use of green chemistry principles, through the Greenness Grid method, or eco-efficiency analysis In this way, different assessing approaches were provided, which allows a greater knowledge and a deeper study of the alternatives of biological scenarios, also including the techno-economic evaluation to determine the suitability of the types of equipment as well as to identify the economic feasibility.

Therefore, this doctoral thesis proposes a series of bio-based scenarios with the objective of evaluating new, more sustainable production models that enhance the use of resources in an integrated manner, thus promoting the circular economy of the supply chain. It is important to note that the term "bio" is not always synonymous with "sustainable", as it implies the development of processes with a much lower degree of optimization compared to more conventional production models based on fossil resources. This fact was demonstrated in most of the chapters of the thesis, where it was verified that in several environmental profiles, energy consumption is the main contributor to the associated impacts, given the lack of energy optimization and the low level of development.

On the other hand, it is worth mentioning that the valorization processes were developed through large-scale models using laboratory data, not at pilot scale, which also implies that the degree of improvement and optimization is high, and therefore also their associated impacts, as well as their economic feasibility. While this series of drawbacks may reduce to some extent the integration of bio-based processes and products in the market, it has been observed that most of the scenarios proposed throughout this thesis are feasible from an economic point of view, a fact demonstrated by performing techno-economic analyses, as well as appropriate from an environmental perspective, having in some cases a lower associated impact compared to conventional production models.

To finalize, it is expected that the results of this thesis can be considered as a further step in the integration of bio-based production processes in the market value chain, to promote the integral use of resources, the valorization of waste and the use of technologies that are more environmentally friendly.

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SECTION I
Introduction

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SUMMARY

The need to adapt production processes to the demands of the population goes beyond increasing production capacities or establishing a business model in line with consumption trends. The growing concern about the uncontrolled consumption of non-renewable resources is already a fact, both from the point of view of societal awareness, advocating more sustainable products and services, and from the regulatory point of view towards the compliance of sustainable development objectives and a decarbonized society with the least possible impact on the environment. In this approach, the development of business models based on the use of renewable resources, the transformation of waste into raw materials and the promotion of circular systems of value generation is increasingly present. The transition from traditionally linear production to models that promote the integral use of resources and the maximum reduction of waste is one of the essential aspects of this transition.

In this perspective, the development of biorefineries can be considered as a key element to promote the substitution of the massive use of fossil resources using renewable resources, as in the case of lignocellulosic biomass. This shift is not only positive for the goal of ensuring the availability of fossil resources in the future, but it is also expected to promote more environmentally friendly production models and, in addition, to endorse the production of a plethora of products from cascade manufacturing systems. However, to effectively show these long-term benefits, it is important to develop sustainability assessments through sustainability holistic evaluations that would be implied by the integration of these models in the value chain.

The first section of the thesis includes an overview of the application of sustainability principles for the evaluation of biorefineries, as well as of the bioproducts that can be obtained in such a productive scheme, adaptable according to the raw materials and the quality of the final products pursued (**Chapter 1)**. A first approach to the concept of circular economy is also included, focusing on how the integral valorization of waste streams could lead to the production of products with high marketable added value (**Chapter 2**).

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1

Sustainability perspective in the context of biorefineries

SUMMARY

On the pathway for achieving resource-efficiency, profitable alternative production models and environmental protection, the life cycle consumption of available resources, as well as the potential for waste generation, are key aspects to be studied and optimized. The objectives of sustainable development seek to focus, or guide, the actual trend of consumption and production towards models more focused on the maintenance of resources and the environment, with a view to maintaining their quality and enhancing their availability in the long term.

In this approach, the implementation of production and management systems based on technologies capable of using bio-based raw materials is considered an appropriate business strategy model with high development potential. The characteristics of raw materials allow the establishment of cascade production systems, i.e., from one resource to obtain multiple products, which is considered as an added value and a more efficient use of the available resources.

However, the introduction of these production models in the supply chain must be implemented through the development of circular economy and sustainability strategies, which must be previously analyzed in order to demonstrate that the process alternatives are more suitable than the existing ones. In this regard, the appropriate selection of the feedstock and/or waste streams as process inputs, the correct process design and the optimization of the operation conditions (i.e. for allowing a higher productivity) are key aspects to be assessed in order to ensure the profitability and effectiveness of the sustainable characterization of the alternative bio-based process.

To this end, **Chapter 1** is focused on the introduction on the importance of advocating for sustainable practices, aiming to fulfill the concepts integrated in the sustainability principles, and how they should be integrated in the design of bio-based production models.

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OUTLINE

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1.1 The concept of sustainable development: its origins and evolution

In the endeavor to achieve carbon neutrality by 2050, a target set through the European Green Deal, a transition of resource consumption and the production of goods and services towards a more efficient and sustainable economy is required, focused on moving from linear to circular production. More efficient use of resources, reduction of waste flows, development of new technologies and innovative process alternatives capable of providing products that comply with the objectives embedded in the pillars of sustainability is needed.

In this approach, it is important that all actors in the value chains are aware of promoting sustainable development, from an environmental, economic and social point of view, where the support of policy makers, stakeholders and consumers are indispensable elements. As the writer J.A. Barker states, "Vision without actions is merely a dream but vision with action can change the world", and the implementation of sustainability principles in the production patterns could help to move from vision to action.

The 1987 Brundtland Report was the first to use the term "sustainable development" defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs".

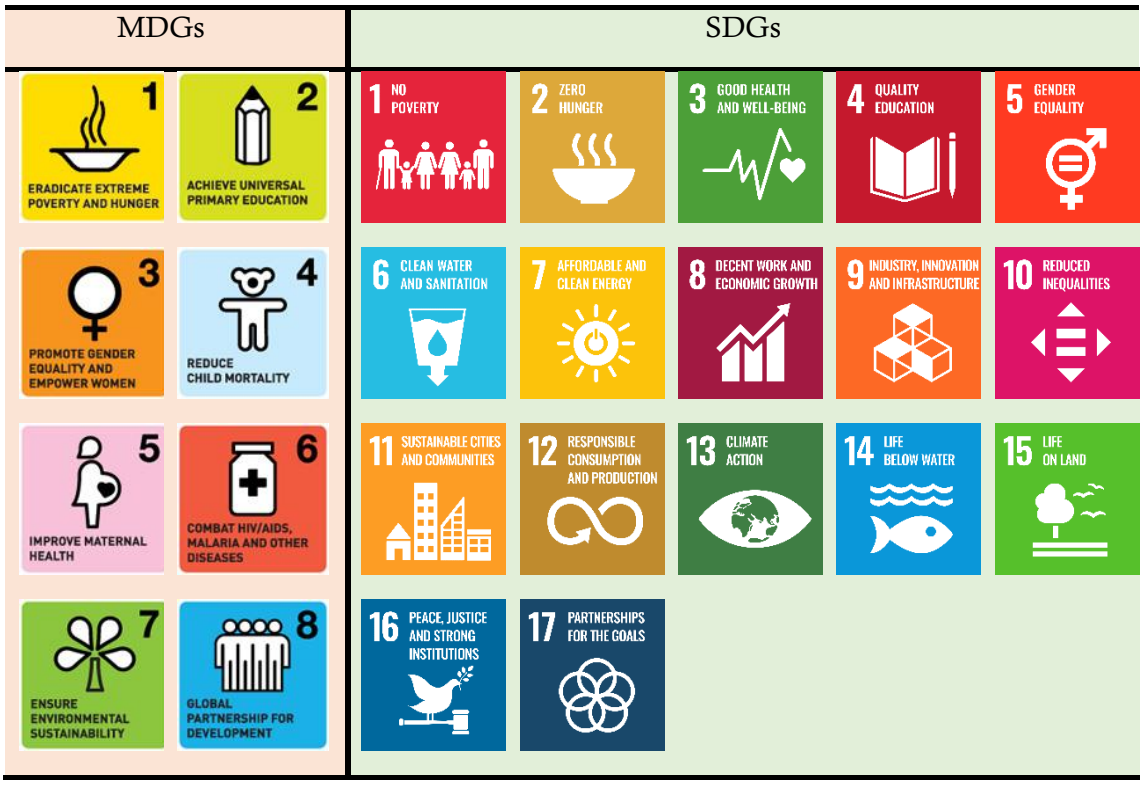
Just five years later, the United Nations adopted the definition at the Conference on Environment and Development in Rio de Janeiro and developed the Agenda 21, as a plan of action to achieve sustainable development through conservation of natural resources, collaborative economic growth and proactive teaching of sustainability at all levels of education. The 1992 conference prompted the creation of the UNFCC (United Nations Framework Convention on Climate Change), and in the same year the UN Convention on Biological Diversity was launched, in which the EU countries signed a commitment to implement the 3 objectives of the convention: conservation of biological diversity, sustainable use of resources, and fair and equitable sharing of the benefits arising from the use of these resources.

Another important agreement derived from the 1992 Rio Earth Summit was the Principles of Forest Management, which includes a series of recommendations to ensure forest protection, management and conservation. In these principles the concept of “the greening of the world” has emerged, based on encouraging planting and conserving the forest lands, controlling the pollutants that are detrimental and promoting a proper forest management under a sustainable approach.

Besides, the Commission on Sustainable Development was also established in 1992 as a “tool” to ensure, guarantee and review the follow-up and proper implementation of the commitment signed on the Rio Declaration on Environment and Development. Besides, it is also a organism helpful for proposing and providing policy guidance, mostly on the scope of the Johannesburg Plan of Implementation (JPOI), an agreement focused on promote the avoidance of the practices that seriously threaten sustainable development.

What are known as the Sustainable Development Goals (SDGs) had its origin in the Millennium Summit, a meeting held in 2000 at the United Nations headquarters in New York. It culminated in the set-up of 8 Millennium Development Goals (MDGs), adopted by 189 member states through the Millennium Declaration (**Table 1**). The SDGs were defined in 2012 at the UN Conference on Sustainable Development in Rio de Janeiro. The main differences among the MDGs and the SDGs are the number of goals, from 8 to 17, and targets, from 21 to 169, the general scope, from social to the three pillars of sustainability, and the shift from focusing on developed countries to broadening their deployment to global implementation.

Table 1.The transition from MDGs to SGDs. Source: Own elaboration.



The degree of achievement and trends in each of the SDGs is different for each country in the European Union, and this is further related to how each region works to improve circularity, environmental protection, economic growth and social welfare. In this regard, the European Commission provides a database to document European sustainable development, for each of the SDGs. The European Union, in 2021, achieves an SDG Index score of 71.4/100, with SDGs 2, 13, 14 and 15 requiring the greatest efforts to go further in sustainable actions.

The regions that achieved higher index score values compared to the European Union average score are those in the north, with an average value of 80.6, while the southern and the central achieved lower scores, 68.3 and 68.0, respectively. On the other hand, considering the current status on the degree of achievement according to each SDG, **Table 2** shows the actual status of each country, denoted “Major challenges” in red, “Significant challenges” in orange, “Challenges remain” in yellow and “Goal achieved” in green.

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Table 2. Growth of development on achieving the goals of the SDG by the European countries. Source: Own elaboration.

	SDG1	SDG2	SDG3	SDG4	SDG5	SDG6	SDG7	SDG8	SDG9	SDG10	SDG11	SDG12	SDG13	SDG14	SDG15	SDG16	SDG17
FIN																	
SWE																	
DNK																	
AUT																	
NOR																	
DEU																	
CHE																	
EST																	
SVN																	
FRA																	
CZE																	
BEL																	
NLD																	
ISL																	
POL																	
IRL																	
GBR																	
SVK																	
LVA																	
PRT																	
HUN																	
ESP																	
ITA																	
HRV																	
LTU																	
LUX																	
GRC																	
MLT																	
ROU																	
MKD																	
SRB																	
CYP																	
BGR																	
TUR																	
EU																	

As can be seen in **Table 2**, most of the regions that are part of the European Union have a very low achievement in the sub-targets identified for SDG13. The rationale behind this is mainly based on the recurrent use of fossil fuels for the production of goods and services and the amount of waste produced, which is generally disposed in landfills or incinerated, instead of being reused and recycled.

Figure 1 provides information at the European level on the sustainable use of resources, as well as on waste management and circularity of the different countries through four indicators: (1) raw materials consumption, (2) generation of waste, (3) circularity material use rate and (4) gross value added in the environmental goods and services sector. The data come from the EC database, using the topics most related to the sustainability approach and were normalized to a scale between 0 and 1, being 1 the score representing the country with the highest value on the specific indicator and 0 the lowest.

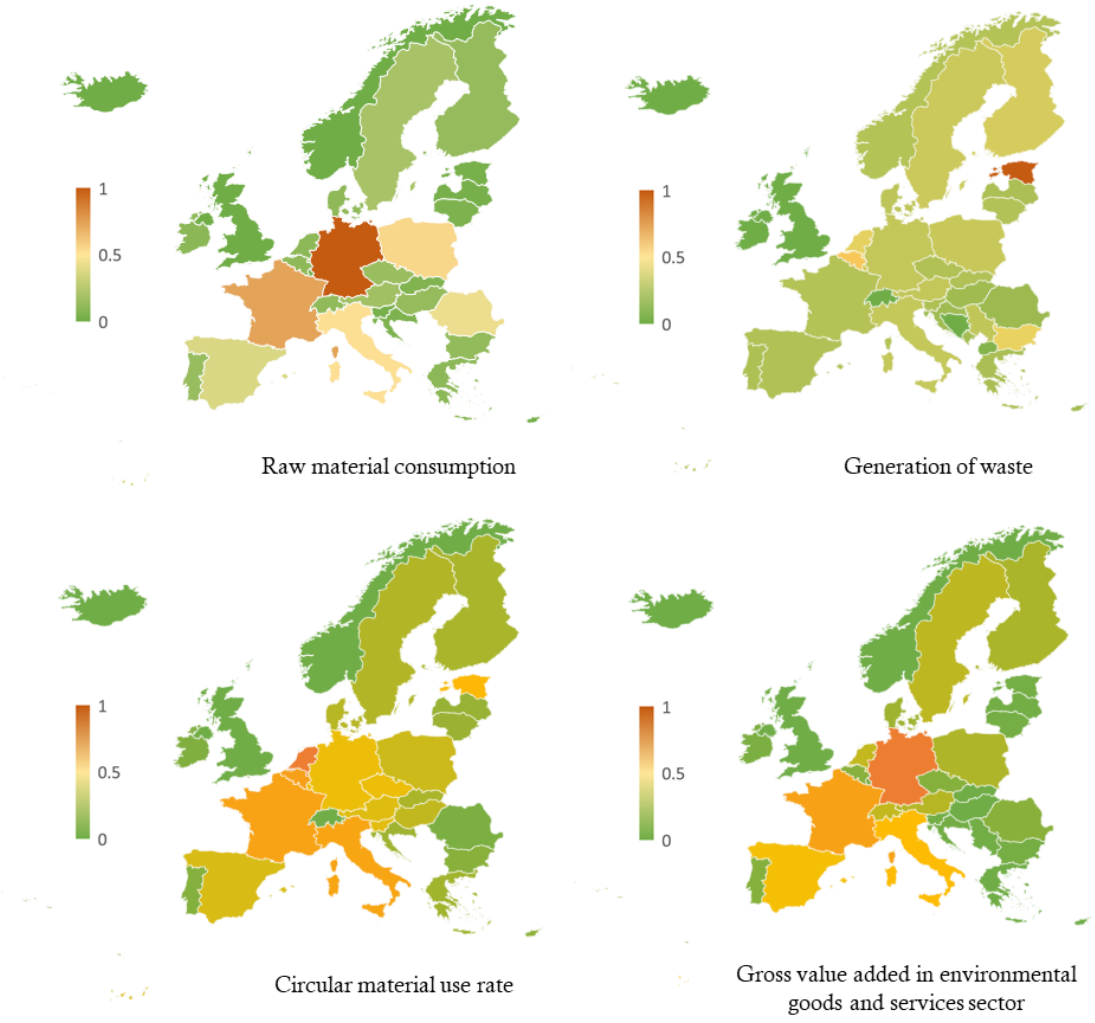

Figure 1. Raw materials consumption, generation of waste, circular material use rate and gloss value added in environmental good and services indicators based on the database of the European Commission, related with sustainability practices and actions in the European context. Own elaboration

The consumption of raw materials is directly related to the efficient use of resources. In this sense, a more sustainable use of resources is being developed, which in turn could be related to the amount of waste generated and the circular use of materials in European regions. The

connection between these three aspects is interesting (**Figure 1**), as the regions with the highest consumption of raw materials are not the ones that produce the largest amount of waste. Given the scores obtained, it could be appreciated that an extensive use of virgin materials does not imply that the production of goods and services is linear, or that it contributes to a greater amount of waste streams produced.

The integration of circularity action plans, which infer an integrated use of resources, and the development of biorefinery facilities with the aim of "reusing" waste streams into raw material streams, helps to ensure that regions with the highest demand for virgin materials are not the least sustainable. Still, extensive consumption of virgin materials could lead to their depletion and associated environmental impacts (e.g., extensive use of forest resources could lead to deforestation, while increased consumption of agricultural raw materials could lead to soil degradation and erosion). Therefore, it is important to develop management and action plans to avoid impacts on the quality and health of the environment.

It is true that reducing the consumption of raw materials is not easy, as it is necessary to respond to the demands of society, but the implementation, management and development of adequate practices in the global value chain of production could be beneficial from the point of view of sustainability actions. This should be the main awareness of production facilities: to be efficient, to be consistent with the consumption of materials and to be conscious of the impacts on society, economic issues and the environment. It is also observed that, in general, those regions that are more worried about the development of more circular production actions are those that achieve gross value in the environmental goods and services sectors. This probably stems from the enhanced development of more sustainable actions, in accordance with regional environmental and sustainability policies and regulations, and, of course, from the acceptance by community members of the production and consumption of bio-based products derived from more sustainable production processes.

1.2 The added value of biorefineries in the valorization of waste and side-streams

Biorefineries are considered strategic sectors based on the use of renewable natural resources (Attard et al., 2020; Stegmann et al., 2020), among which lignocellulosic biomass stands out, given its wide spectrum of application and availability (Hassan et al., 2019; Lange et al., 2021). Biorefinery design strategies must take into account process stream compositions, equipment and operating conditions that ensure high efficiency and cost-effective production. Biorefineries are expected to contribute to the future development of sustainable, clean and renewable energy and products (Cherubini et al., 2009). To this end, best available techniques and powerful process modelling tools/software should be applied in the definition of biorefinery approaches. In terms of feedstocks for biorefineries, these could be classified into "dedicated energy crops", for those that are used entirely for energy production, and in the case of those focused on "biomass waste valorization", other high value-added co-products could be obtained (Chaturvedi et al., 2020). Regarding the classification of biorefineries, a distinction is made between "energy-driven biorefineries" for the first category of feedstocks and "product-driven biorefineries" providing chemicals, organic acids, biopolymers, bioproducts and biofertilizers (Aristizabal-Marulanda et al., 2017)**.** Another important fact about biorefineries is that most process models are at an early stage of development, and the technology readiness level (TRL) is not high enough to guarantee market potential. Before launching a large-scale biorefinery production plan, process modelling and technical feasibility approaches need to be addressed (Mukherjee et al., 2022; Xu et al., 2021).

The development of biorefineries is envisioned as a win-win approach, bearing in mind that their viability relies on the efficient use of all the components of the lignocellulosic biomass

(Liu et al., 2022). Its multi-production capacity is intended to enhance economic profitability and encourage the penetration of circular actions in the manufacture of bio-products (Culaba et al., 2023).

On the other hand, it is important to keep in mind that although the integration of biorefinery facilities within the economic chain does not imply a contribution to the improvement of all the 17 SDGs, it does have a relevant contribution to achieve the objectives of more than one of them. Particularly, there is an outstanding involvement in SDG 7 (given the production of clean energy through the use of biomass, thus avoiding the consumption and harmful effects derived from the use of fossil resources), 9 (development of emerging innovative technologies directly focused on favoring the integral use of lignocellulosic-based resources), 12 (as biorefineries favor circular actions through the use of waste flows as feedstocks) and 13 (due to the positive effect of biorefineries on the environment and on the reduction of climate change).

Certain contributions can also be identified for other SDGs, although perhaps not as direct, as in the case of SDG 3, since encouraging more sustainable production patterns would imply a lower negative effect on the environment and, therefore, lesser harmful effect on human health. It applies similarly for SDG8, since the use of waste to obtain high value-added products can be considered as an economically viable business strategy, as well as for SDG11, since the development of biorefineries have a positive impact on the sustainability of the surrounding communities, both from an environmental, economic and social point of view, for example through the creation of job opportunities.

Within a biorefinery facility, lignocellulosic wastes are converted into valuable bioproducts through the valorization of waste and side-streams, avoiding the impacts derived from end-of-life treatments or disposal (Ali et al., 2022; Sauer et al., 2014). On the other hand, the selection of one type of biorefinery or another will depend on the characteristics, the availability of resources depending on the type of waste handled, the available technology and the market penetration potential of the bioproducts (Nizami et al., 2017; Saha and Mukhopadhyay, 2020).

In this sense, future biorefineries should be developed considering the integral use of biomass feedstock, to meet circular economy criteria on waste reduction, making full use of available resources and ensuring market opportunities for bioproducts, taking into account both demands and competition with their counterparts. Several reports have evaluated the use of food waste, lignocellulosic waste, municipal solid waste, paper waste and manure as the main bio-based resources to produce chemicals, biofuels and bioplastics, among others (Khatami et al., 2021; Lettner et al., 2018; Sepúlveda et al., 2021).

The development of biorefineries has intensively increased in the last decade based on the valorization of waste streams instead of directly using virgin renewable materials (Parada et al., 2018). On the other hand, the development of biorefineries could help to promote rural and regional development, a key factor when assessing the social pillar of sustainability, and to avoid reliance on delocalized resources and goods in the global value chain (Muntoni, 2019; Parada et al., 2018).

The potential of biorefineries is expected to grow in the coming years, as it is estimated that the demand for bioproducts could reach 113 Mt/year by 2050, expecting an annual growth rate of 15%. It has been reported that, approximately, $5 \cdot 10^5 - 7 \cdot 10^5$ t/year is the minimum production capacity to ensure the potentiality of biorefineries in the market, a threshold that could be reduced when waste streams are used as inputs (Muntoni, 2019). However, some authors have claimed that the development of small-scale biorefineries can also bring economic, environmental and social benefits, associated with incentives for the management of

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agricultural waste in a nearby environment and job creation (Solarte-Toro and Cardona Alzate, 2021).

The most used feedstocks for multiproduct biorefinery are agricultural, followed by forestry and waste (**Figure 2**). The reason behind this is that most of the biofuels currently produced are first generation, so crops are harvested directly for energy rather than for food production. Given the controversy over the food and biofuels binomial, the transition to second and third generation biofuels and bioproducts, using forests, waste streams and marine resources is becoming more urgent.

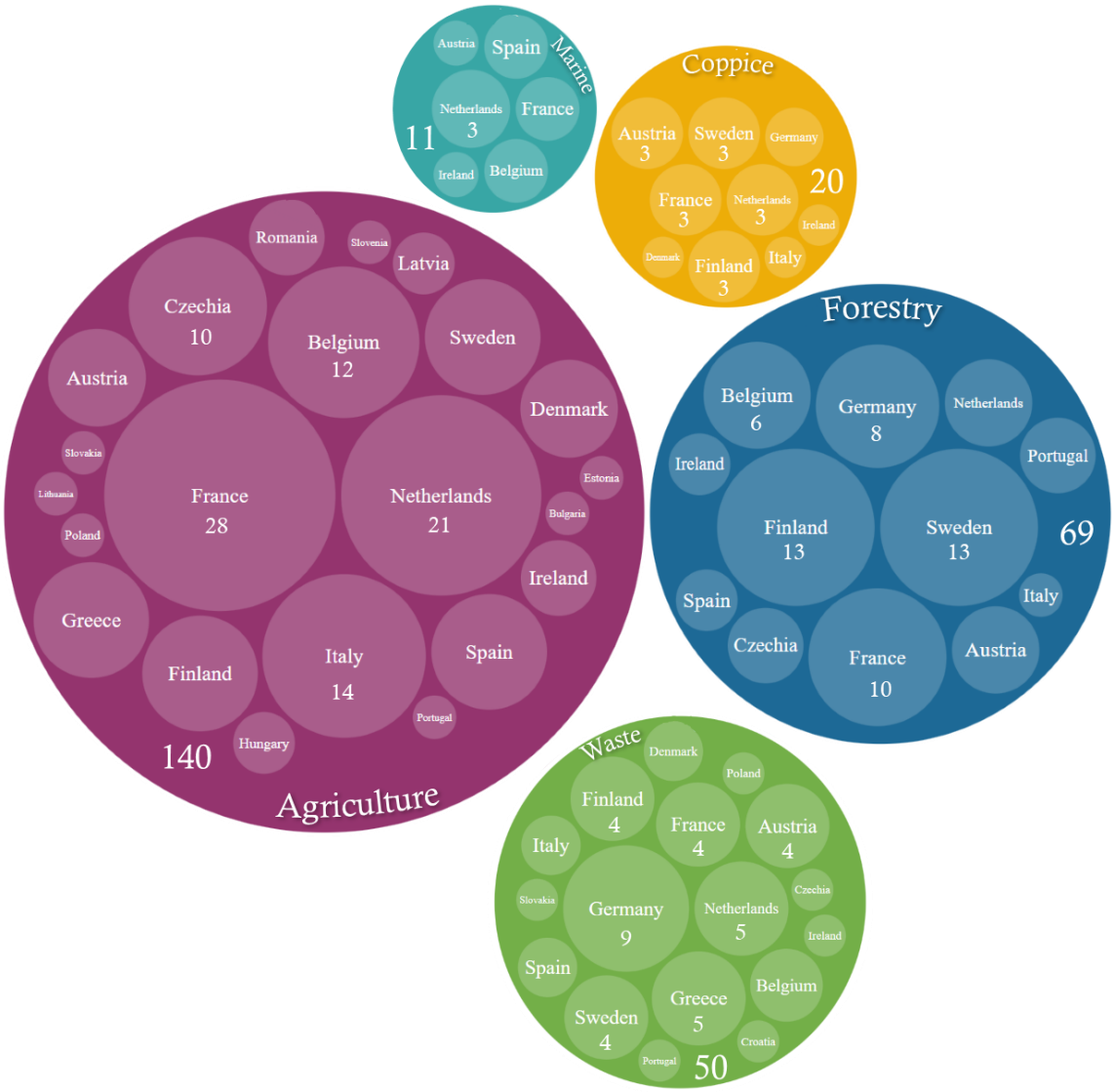

Figure 2. Feedstock used for multiproduct biorefineries in the European context. Own elaboration based on the EC database (Parisi et al., 2020)

On the other hand, instead of focusing only on the type of feedstock, it is also important to analyze the type of products obtained. As depicted in **Figure 3**, the bio-based product that stands out is chemicals, followed by biofuels and the production of composites and fibers, with Germany as the region that stands out, followed by France and the Netherlands. Examples

include Alberta Pacific Forest Industries, which uses wood as a feedstock to produce not only pulp, but biomethanol, heat and electricity, with a processing capacity of 765 ktons of wood/day. In terms of multiple bio-based feedstocks in the same production plant, Maabjerg Energy uses wood chips, manure, sewage sludge, municipal solid waste and straw as feedstocks to co-produce biomethane, bioethanol (approx. $8 \cdot 10^4$ m^3 /year), fertilizer, electricity and heat. Another example of this multiple production scheme is ZeaChem, which uses various cellulosic feedstocks (wood waste, wheat straw, corn stover) to produce bioethanol and ethyl acetate ester, with a process capacity of 10 tons/day (Cardona-Alzate et al., 2020).

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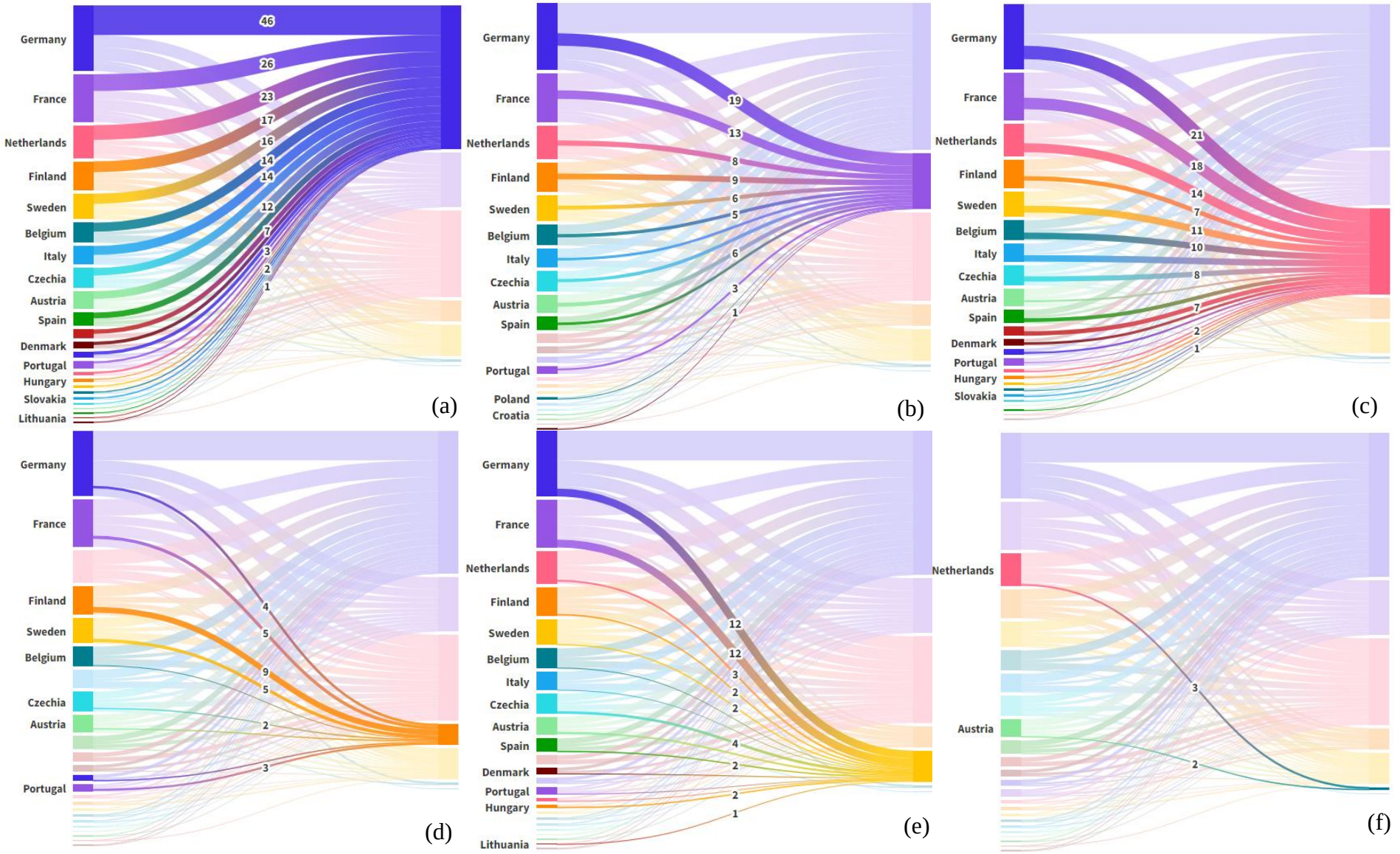

Figure 3. Multiproduct biorefineries in Europe. (a) Chemicals (b) Composite and fibers (c) Liquid biofuels (d) Pulp & paper (e) Starch & sugar (f) Biomethane

1.3 Accounting for sustainability: metrics and indicators

On the subject of measuring the sustainability indicators of a scenario, the Sustainability Accounting Standards Board (SASB) has developed a guideline to evaluate the subset of social, environmental and governance indicators that are directly related with a specific industrial sector. The typology most related to the approach addressed in this thesis is related with the "Renewable Resources & Alternative energy" (RR&AE) and "Resource transformation" (RT), where a specific sustainability profile is available for forest management, biofuels and pulp and paper products for the RR&AE typology, and containers & packaging and chemicals for the RT group. **Table 3-Table 5** include a brief summary of the topics and accounting metrics used for the assessment of the products subsequently analyzed in this thesis document. **Table 3** includes the environmental issues, **Table 4** the management issues and **Table 5** the ones related with social and economic issues.

Table 3. SASB according to the products and processes assessed on the thesis. Environmental issues. Own elaboration based on SASB information.

Typology & sector		Products	GHGs	Air emissions measures	Feedstock	Ecosystem protection
RT	(1)[1]	Polymers, adhesives, resins, agri-chemicals	Measurement of short and long-term emissions	NO_x, SO_x, VOCs and HAPs	—	—
	(2)[1]	Food packaging	Measurement of short and long-term emissions.	NO_x, SO_x, VOCs and PM	—	Strategies to reduce environmental impact of packaging
RR & AE	(3)[1]	Timber	Strategies for adapt and mitigate climate change	—	—	Area of conserved/threatened species forestland, land productivity.
	(4)[1]	Wood pulp and paper	Measure/analysis of short and long-term emissions	NO_x, SO_x, VOCs, PM and HAPs	—	—

[1]Note: (1) Chemicals (2) Containers & packaging (3) Forestry management (4) Pulp & paper products

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Table 4. SASB according to the products and processes assessed on the thesis. Management issues. Own elaboration based on SASB information

Typology & sector		Energy	Water
RT	(1)[1]	Consumption, amount of renewable/self-produced energy	Total water consumed/withdrawn, water quality and risk management
	(2)[1]	Consumption, amount of renewable/self-produced energy	Total water consumed/withdrawn, water quality and risk management
RR & AE	(3)[1]	—	—
	(4)[1]	Total energy consumed, amount of biomass-based energy and use of renewable resources	Total water consumed/withdrawn, water quality and risk management

		Hazardous waste	Legal & Regulations	Supply Chain
RT	(1)[1]	Amount of hazardous waste and percentage recycled	Address environmental and social issues	—
	(2)[1]	Amount of hazardous waste and percentage recycled	—	Total wood fibers/aluminum used from certified resources
RR & AE	(3)[1]	—	—	—
	(4)[1]	—	Rights of indigenous people	Wood fiber source, amount of recycled and recovered fiber

[1]Note: (1) Chemicals (2) Containers & packaging (3) Forestry management (4) Pulp & paper products

Table 5. SASB according to the products and processes assessed on the thesis. Social and economic issues. Own elaboration based on SASB information

Typology & sector		Social			Economic
		Community relations	**Workforce Health & Safety**	**GMOs**	**Product efficiency**
RT	(1)[1]	Assess processes, risk and care of social interests	Job creation, health care, number of incidents. Amount of hazardous chemicals in the products	Percentage of modified organisms per product	Revenues by consumers' product acquisition
	(2)[1]	—	Recalls issues and analysis of concerning emerging materials	—	Revenues by consumers' product acquisition
RR & AE	(3)[1]	—	—	—	—
	(4)[1]	—	—	—	—

[1]Note: (1) Chemicals (2) Containers & packaging (3) Forestry management (4) Pulp & paper products

On the other hand, it should be taken into account that the concept and the idea of sustainability is considered as the fundamental issue for the bioeconomy, as it is constructed on the rationale of creating value and benefits in a long-term approach. In fact, the EU has developed a bioeconomy strategy to assess and be aware of the environmental drivers on the different production sectors. This strategy is based on the premise of promoting an efficient use of resources, appropriate management and beneficial policies and production scenarios for the integration of bio-based

manufacturing models in the economic value chain (Prieler et al., 2019). Regarding policies, its implication on the effective penetration of biorefineries is essential, based on the enhancement of green economic growth, the foundation on the development of innovative technologies and the encouragement of developing economic value that complies with economic, social and environmental issues, i.e. the three pillars of sustainability.

1.4 The significance of assessing sustainability on present and future scenarios

The need to integrate the sustainability assessment of a production system is already a reality. Directive (EU) 2022/2464 of the European Parliament and of the Council has recently been published, focused on the definition of new sustainability constraints for the productive sectors. It includes more detailed requirements in terms of the capacity to cause environmental impact, as well as the economic and social implication that a production sector or manufacturing process may entail. Its principles have been built on the basis of the objectives established by the EU on the Climate Action, and it is considered as a great step forward towards the development of more adequate and precise standards in the search for sustainability at a global level.

In this context, the evaluation of the damage potential of a productive activity under the approach of the search for sustainable development becomes a necessity, both at corporate and socioeconomic level, and even for the development of new political strategies. However, it is important to mention that, among the three pillars of sustainability, the most developed methodology is the one that involves the evaluation of the degree of environmental suitability (i.e. Life Cycle Assessment, LCA), followed by economic feasibility studies, through techno-economic assessments (TEA), among others.

On the other hand, as the approach to the development of social assessments is not fully defined, there is no well-defined methodological guide for their development. In addition, the lack of sector-specific data and the need to use generic databases by region or country considerably reduce the degree of precision and representativeness of the results. For this reason, in this doctoral thesis dissertation both environmental and economic assessments of the scenarios under study are presented, under the premise that economic evaluations are carried out as long as (1) data is available for their development, (2) a large-scale modeling of the process has been conducted, and (3) studies on the economic evaluation of traditional processes, based on the use of fossil resources, are available for comparison.

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2

Turning problems into opportunities: from biowaste and natural resources to added value bioproducts

SUMMARY

The most widely implemented waste management strategies are focused on energy recovery, such as incineration, or landfilling. As can be envisioned, the potential impact, especially of the latter strategy, is very high and should be limited only to those wastes for which recovery and management routes do not offer viable alternatives. In the global context of waste management, the development of strategies that promote the integrated use of available resources, is already a present need and a future obligation, given the sustainable development objectives to be achieved, as well as compliance with new policies.

Therefore, **Chapter 2** is presented as a prelude to the different valorization strategies proposed throughout this thesis, focused on the definition of biowaste and natural resources to be used as raw materials in the following Chapters, seeking the development of biotechnological and biorefinery strategies based on the principles of sustainability and circular economy.

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2.1 Food Waste and Circular Economy: challenges and opportunities.

According to the Food and Agriculture Organization of the United Nations (FAO), one third of the products that have the quality to be consumed by humans are directly wasted or lost annually (FAO, 2013). The low efficiency of some food supply chains, the food disposal by consumers and the lack of comprehensive food use by the service sector, such as catering or supermarkets, has led to the exorbitant amount of food discarded year after year (Hadj-Saadoun et al., 2021). It is true that little by little the service sector is promoting initiatives to ensure its consumption by reducing the selling price of the product, or through the use of platforms such as "*Too good to go*", which encourages the reduction of food waste.

The agri-food supply chain is the sector that suffers most from food waste production, representing 37.75% of the total waste generated in the European Union in 2020, according to the Eurostat database. The following graph shows the amount of food waste produced in European countries by 2020, differentiating five main categories: primary sector (agriculture, fisheries and aquaculture), secondary sector (manufacturing and retail of food and beverage products) and tertiary sector (food services and household activities). The values have been normalized according to the total food waste production, i.e., to calculate the contribution of food services, it has been divided over the total food waste produced, and the same procedure for each of the elements represented in **Figure 4.**

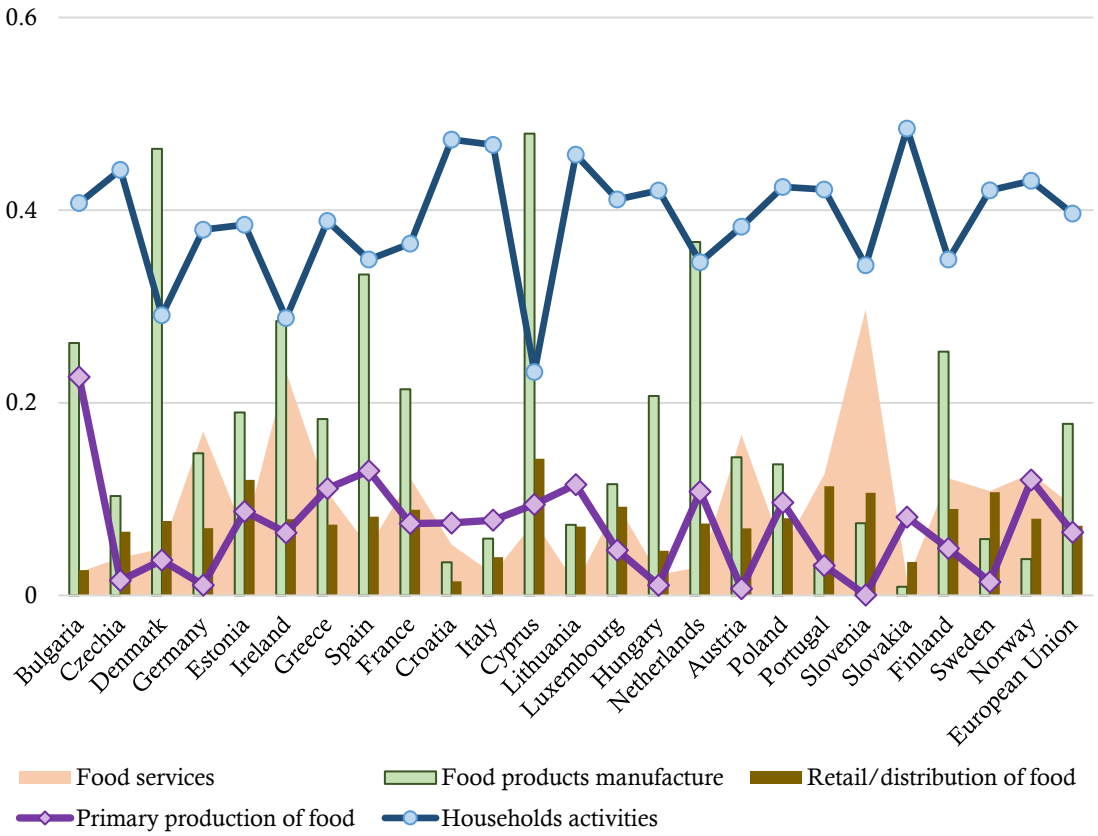

Figure 4. Food waste production categorized by sector. Database: Eurostat

As can be seen, in most EU countries, household activities are the main source of food waste production, i.e., organic waste, which is subsequently managed by municipal waste collection services. However, in two countries in particular (Denmark and Cyprus),

this trend is modified, as it is the production process of food products that leads to the largest amount of waste. On the other hand, in Ireland, Spain and the Netherlands, there is a similar amount of waste production between the primary sector and the industrial production sector.

With regard to food services, such as catering, i.e., the tertiary sector, Ireland, Germany, Austria and Slovenia are the countries with the highest tendency to food waste, where, on the other hand, with the exception of Ireland, waste production by the primary sector is practically zero. At this point, Bulgaria is the country where the management by the primary sector seems to be the least adequate in the search for the integral use of food products, followed by Lithuania, Norway, Spain, Greece and the Netherlands. It is important to take into account that primary production activities in these countries are above average, which may result in higher waste production compared to other countries, where the primary sector is not so strongly involved in their GDP.

To this end, given the trend towards population growth and the need to reduce the amount of waste generated, the implementation of strategies that favor the integral use of food, the reduction of losses and the environmental impacts produced by the enormous amount of waste streams is becoming one of the main objectives within the European strategies to achieve sustainability and circularity in the agri-food sector. However, the agri-food sector is not the only concern in the waste production chain; the forestry sector also produces significant waste streams that need to be managed (OECD, 2021).

2.2 Food Waste as a Source of Value-Added Industrial compounds

The direct disposal of waste entails the loss of the possibility of obtaining economic value from its valorization. In this regard, the implementation of circular economy strategies contributes to sustainability, as the entire forestry and agri-food supply chain will be able to recover and reduce the consumption of resources.

Most waste is handled through landfilling (about 46%) and incineration (24%), two management practices that have been shown to cause significant environmental damage, in addition to preventing the integral use of these waste streams (Nattassha et al., 2020). The waste management hierarchy gives priority to waste reduction at the source of the production and distribution chain, while composting and disposal are the practices that imply the lowest preference in the hierarchy (Kaim, 2021). But, for the time being, the main efforts should focus on developing new strategies to favor waste reduction through the valorization of waste streams, as continuing with the high volume of waste produced will pose a problem in the near future, both for the environmental, social and economic pillars of sustainability.

In addition to promoting new waste management processes, it is equally important to evaluate them thoroughly to ensure that these valorization does not have a more negative impact on the environment than the usual management of energy conversion or landfill. This has been the main focus of this doctoral thesis, in which different valorization strategies are proposed using various waste streams, including agricultural, forestry and industrial waste, and subsequently evaluated under a life cycle assessment perspective (**Figure 5**).

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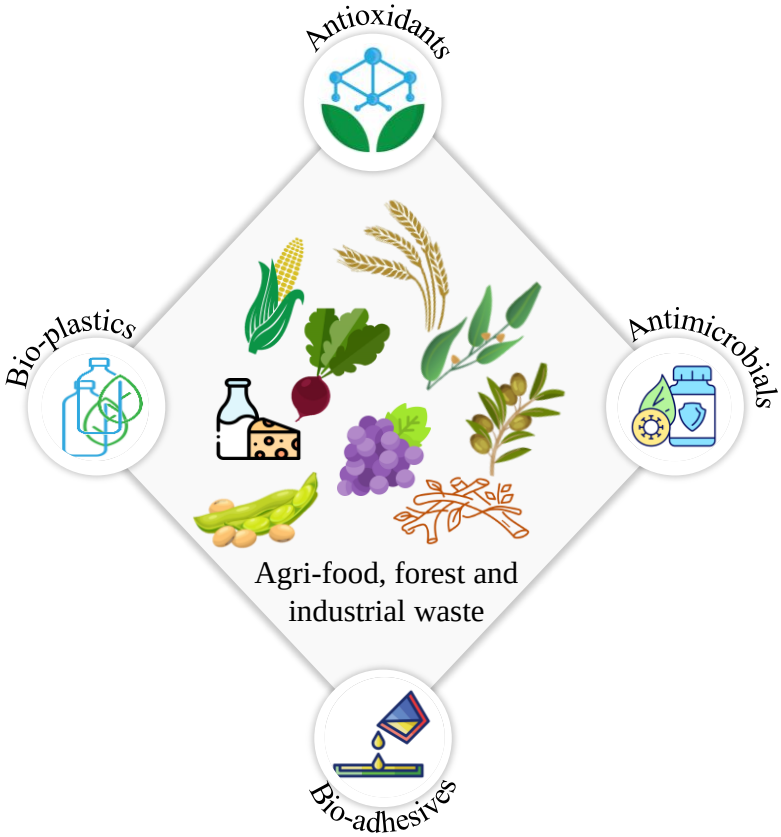

Figure 5. Illustration about the main feedstocks and biorefinery products assessed in the thesis dissertation.

In particular, **Table 6** presents each of the valorization routes that have been evaluated, including the waste streams and the product(s) obtained, also including the Chapter on which is found a detailed description and analysis of each one of them.

Table 6. Valorization routes assessed in the thesis dissertation.

Waste stream	Category	Valorized product	Thesis chapter
Kraft liquor	Lignocellulosic	Wood bio-adhesive	5
Organosolv liquor	Lignocellulosic	Wood bio-adhesive	5
Forestry residues	Lignocellulosic	Wood bio-adhesive	5
		Antimicrobial	8
		Antioxidant	13
Olive pruning	Lignocellulosic	Antimicrobial	8
Soybean residues	Agricultural/industrial	Wood bio-adhesive	6
Corn starch	Agricultural/industrial	Wood bio-adhesive	6
Corn stover	Agricultural/industrial	Antimicrobial	7
Cheese whey	Industrial	Antimicrobial	7
		Antioxidant	13
Sugar beet pulp	Industrial	Antimicrobial	7
Wheat straw	Agricultural/industrial	Active bio-packaging	9/10
Sugar beet	Industrial	Antioxidant	12
Wine residues	Industrial	Antioxidant	13

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2.2.1 Wood bio-adhesives

Wood has been used for decades as a natural raw material to produce various goods and services. Its numerous properties has made this bioresource one of the most demanded and used material for multiple industrial sectors, comprising the production of wood panels, furniture, plastics, leather, textiles and biofuels (Ali et al., 2024). It is a renewable resource with a complex polymeric structure consisting of lignin, cellulose and hemicellulose that is and has been widely used for the production of a wide range of products (Berglund et al., 2020).

On the one hand, a benefit related to the use of wood as a raw material is attributed to its role as a carbon sink in the development of the tree population (Ruter et al., 2008). Thus, it is established that for each cubic meter of wood, approximately 1 ton of CO_2 is stored. On the other hand, the use of wood as a raw material for manufacturing activities leads to a reduction in the use of non-renewable fossil resources, thus avoiding the environmental impacts associated with its extraction, transport and processing activities.

One of the sectors in which its use is most widespread is in the field of wood panels such as plywood, fiberboard and particleboard, among others (Zhang et al., 2019). But, in contrast with the aforementioned benefits, a number of drawbacks associated with the manufacture of panel products have also been listed, mainly due to the use of certain chemicals such as synthetic-based adhesives required in the gluing phase of the boards. The most extensively adhesive used in plywood and particleboard is urea-formaldehyde (UF) (Pocius, 2012), and in the case of fiberboard products, phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF) adhesives are the most widespread (Mathias et al., 2016). More than half of the total world production of formaldehyde is consumed for the manufacture of UF, MUF, and PF adhesives used in wood-based panels.

The high functionality of adhesives in relation to their excellent bonding properties and board quality and strength gives them a dominant position, which greatly hinders the introduction and development of natural-based, renewable adhesives that do not include formaldehyde in their formulation. Nonetheless, the fact that adhesive manufacturing processes are fully optimized based on the operational conditions of pressure, temperature, and curing time certainly gives them a competitive advantage over new developments.

However, research and development on highly functional adhesives capable of replacing formaldehyde-based adhesives has become a necessity given the need to adapt to regulations limiting formaldehyde and volatile organic compounds (VOC) emissions at different stages of the life cycle of wood-based panels (Salem and Böhm, 2013). In particular, the International Agency for Research on Cancer classified formaldehyde as a carcinogenic substance for humans (Popović et al., 2020).

Investigating in more detail the stage associated with the manufacturing process, the main direct and indirect emissions have been identified in a life cycle assessment study of petrochemical adhesives (Wilson, 2010). Thus, the amount of formaldehyde released as an emission derived from the manufacturing process is established at values around $7 \cdot 10^{-3}$ mg/kg adhesive for emissions to air, and up to 10 times higher: $78.4 \cdot 10^{-3}$ mg/kg for emissions to water. In addition to direct emissions, greenhouse gases (GHGs) associated with energy and fuel requirements, as well as emissions of other VOCs, methanol and phenol, stand out.

The negative effects derived from the use of formaldehyde as a bonding agent in the wood panel industry, the obligations derived from environmental and health regulations, as well as the need for innovation, development and research of new natural products with

the aim of reducing the consumption of fossil resources, are the main factors driving the substitution of formaldehyde-based adhesives with bio-adhesives.

In addition, there are numerous studies proposing the development of new bio-based adhesive formulations for use in the gluing phase of panel manufacturing, such as those based on lignocellulosic biomass (including Kraft and Organosolv lignins) (Antov et al., 2021; Aziz et al., 2019; Chen et al., 2020; Gadhave et al., 2019), tannins (condensed and hydrolyzed) (Chen et al., 2020; Tomak and Gonultas, 2018; Zhou and Du, 2020), soybean (soybean, soybean meal, and soy protein) (Chen et al., 2017; Eslah et al., 2016; Li et al., 2017) and starch (corn) (Chen et al., 2019; Gu et al., 2019; Li et al., 2020; Sun et al., 2018).

Among the extensive literature consulted, a common feature is observed among the diversity of research articles, the research has been developed at laboratory scale, with a focus on the chemistry for the formulation of bio-adhesives, as well as the characterization of the developed products and the study of the mechanical properties of the boards. But, in contrast, no significant number of references addressing the production process of bio-adhesives at pilot or industrial scale were found, along with the absence of environmental and techno-economic assessments to identify their potential to be implemented in the market value chain (Arias et al., 2021).

For this reason, in **Chapters 5** and **6**, bio-adhesive alternatives to replace formaldehyde-based adhesives are studied from the point of view of a large-scale production capacity, with the objective of proposing comparative scenarios to the current synthetic production schemes, and also including their environmental assessment. Specifically, **Chapter 5** emphasizes on the use of lignocellulosic-based raw materials and those derived from the pulping process of paper production, such as Kraft and Organosolv lignins. On the other hand, in addition to these types of raw materials, there are other alternative raw materials that have also proven to be efficient for use in the formulation of wood adhesives, as in the case of waste from the forestry and agri-food sectors. Explicitly, in **Chapter 6**, the simulation and environmental evaluation of bio-adhesives based on soy, tannins and starch is evaluated. This selection has been made on the basis of a detailed literature evaluation on the availability of data for their large-scale simulation. Furthermore, these raw materials showed a high potential for the development of bio-adhesives for wood, providing a resin with bonding and thermogravimetric properties that, in addition to complying the requirements established in the standards, are analogous to those offered by formaldehyde-based synthetic resins.

Lastly, in order to evaluate the adequacy of the bio-based adhesives proposed, apart from the LCA, also an assessment based on a planetary level is being evaluated. This is the main focus of **Chapter 7**, in which the bio-adhesives assessment is taken to a planetary level by means of the implementation of the planetary boundaries methodology, for which not only the thresholds established for each impact category have been considered, but also various allocation methods, both economical, as well as production capacity and also related to environmental aspects.

2.2.2 Antimicrobials

Nowadays the fact that consumers perceive a product as natural is a decisive purchasing incentive. Thus, natural products are often minimally processed foods. It seems that "no artificial ingredients", "no additives" and "healthy" are the three most frequent associations in the consumer's mind with the word "natural". The real food movement is booming, which focuses on the absence of ultra-processed/ non-natural products in the diet. However, to avoid the presence of pathogenic microorganisms in

food, it is necessary to add preservatives, most of which are chemical-based and could pose a health risk.

In this context, the use of natural bio-preservatives is a noteworthy alternative, within which bacteriocins play an important role, since they are not harmful to human health (Abbasiliasi et al., 2017) and are also odorless, tasteless and colorless, so they could be added to food products without altering their main properties (Soltani et al., 2020). By avoiding the use of chemicals and heat treatments for food preservation, foods with better organoleptic and nutritional properties are obtained, which is a great advantage given the growing consumer demand for products with less industrial processing and higher nutritional quality (Banerji et al., 2022; Quichaba et al., 2022; Wu et al., 2023)

Bacteriocins are heterologous antimicrobial peptides released extracellularly by Gram + and Gram- bacteria and, in some cases, also by *Archaea* (Abbasiliasi et al., 2017; Lopetuso et al., 2019). They can trigger an inhibitory activity in the presence of undesirable microorganisms, including bacteria of the same genus and unrelated pathogens, such as *Clostridium* or *Listeria* (Malvido et al., 2019). Class I bacteriocins (*lantibiotics*) are small peptides that undergo extensive post-translational modification to produce the active peptide.

Nisin, the most studied bacteriocin, belongs to the Class I bacteriocins, which are active against a broad spectrum of pathogenic bacteria. The dose of nisin required to obtain the desired effect depends on several factors, including processing and storage conditions, carbon source, chemicals, bacterial load and product formulation. Because of their potential use as natural preservatives, bacteriocins produced by lactic acid bacteria have been the subject of intensive research in recent years. In particular, Nisin A has been classified as Generally Recognized as Safe (GRAS) by the US Food and Drug Administration (Özel et al., 2018) and recognized by WHO (World Health Organization) for the food industry (Cano-Serna et al., 2015). Although nisin is considered a high-quality preservative for food processing and preservation, the costs associated with its production process are high, up to US$ 770 for 25 g additive containing 2.5% of pure nisin (Guerra et al., 2007; Özel et al., 2018).

The lack of economic profitability is one of the main reasons of the widespread use of nisin in the food sector, given the high cost of the commercial culture medium required for its formulation (Guerra et al., 2007; Özel et al., 2018). In this regard, with the aim of addressing a more efficient nisin production, it is essential to tackle the coupling of biotechnology and circular economy approach, through the development of a biorefinery production scheme.

With this in mind, the microbial production of nisin from waste streams emerges as an interesting and profitable approach. In this sense, the valorization of both agri-food residual streams and lignocellulosic residues as sources of fermentable sugars would significantly reduce the costs associated with the process, in addition to providing an innovative model of circular biotechnological production.

For this purpose, several alternatives have been considered as raw materials for the subsequent production of nisin: cheese whey, corn stover, sugar beet pulp, eucalyptus and olive pruning residues from the agri-food sector in **Chapters 8** and **9**. The selection of these materials has been based on three main reasons: (1) the availability of bibliographic data for the development the full-scale conceptual design and (2) the gross quantities for these agri-food residues produced annually and the lack of valorization strategies to manage and recover them and (3) their adequate composition in sugars, nitrogen compounds and proteins to be used as a substrate.

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2.2.3 Active bio-packaging

In response to the trends in consumption habits, the agri-food industry has progressively implemented production and preservation technologies that guarantee the hygienic quality of food towards the use of biodegradable packaging systems that displace the massive use of plastic (Al-Tayyar et al., 2020; Gopalakrishnan et al., 2021; Kouhi et al., 2020). According to data from the European Bioplastics Association, the global production capacity of bioplastics will increase from about 2.11 million tons in 2020 to approximately 2.87 million tons in 2025. Among the different types of biopolymers, the group of biodegradable plastics, including PLA (Poly lactic acid), PHA (polyhydroxy alkanoate), starch blends and others, account for the largest share with almost 60% (more than 1.2 million tons) of global bioplastics production, which will facilitate the supply of raw material for various industrial sectors and the possibility of lowering their price.

The ability to be biodegradable, compostable, low-cost manufacturing and environmentally friendly have made PLA biofilms good candidates for the development of food packaging films. However, certain strengthening strategies must be considered when it comes to using such biofilms as food packaging materials. Barrier properties, i.e., water and heat resistance, must be improved to ensure adequate food preservation. However, there are studies that address the development of techniques that, in a simple way, can significantly improve these weaknesses, without forgetting the "bio/natural" concept. For example, the addition of bio-nanocomposite materials in biofilm shows that water resistance can be increased by 60% (El Bourakadi et al., 2021; Hong et al., 2021; Ivankovic et al., 2017).

Beyond the traditional "packaging" approach, new food preservation technologies are emerging under the umbrella of "active packaging" (Akhter et al., 2019; Chen et al., 2021; Monjazeb Marvdashti et al., 2019). These are systems designed to intentionally incorporate components that release beneficial substances such as antimicrobials, antioxidants, flavorings, or absorb substances from the packaged food or its environment, such as unwanted or harmful substances like oxygen, moisture, or unpleasant odors. Through the technological development of active packaging systems, it is possible to correct the shortcomings of traditional preservation technologies for packaged foods, improving their quality, extending their shelf life and avoiding food waste (Al-Tayyar et al., 2020; Hong et al., 2021; Ivankovic et al., 2017; Kouhi et al., 2020).

In addition to the potential of bioplastics as a food packaging material, there is a renewed interest in fresh and "natural" products, i.e., products without artificial additives and preservatives that retain their nutritional and organoleptic properties after processing. Beyond thermal processes and chemical additives, bacteriocins emerge as potent antimicrobial agents and offer the possibility of preserving foods and especially their organoleptic quality. In fact, several research articles have evaluated the use of nisin to produce functional food packaging materials, reaching its efficacy against foodborne pathogens (Jin and Zhang, 2008; Mauriello et al., 2005; Saini et al., 2016; Santos et al., 2018). In particular, nisin stands out not only as a natural bio-preservative (Chen et al., 2021; Monjazeb Marvdashti et al., 2019) but also in the biomedical and pharmaceutical field as it reduces the undesirable effects of certain antibiotics (Ellis, 2018) and is effective in the treatment of infections related to drug-resistant, gastrointestinal and respiratory pathogens, among others (Shin et al., 2016). As an example of cutting-edge research, the inclusion of bacteriocins in nanomaterials has shown positive preliminary results as a potential anti-cancer treatment, reducing the growth of tumor cells (Naskar and Kim, 2021).

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In this regard, **Chapter 10** addresses the environmental evaluation of the production process of functional biofilms based on PLA and nisin from the valorization of wheat straw as a source of fermentable sugars after enzymatic hydrolysis of the cellulose available in the biomass. The reason for choosing this biotechnological strategy is in line with that mentioned above for **Chapters 8** and **9.**

On the other hand, related to the development of bio-based active food packaging, a multi-criteria roadmap based on holistic criteria together with quantitative metrics is included in **Chapter 11** to assess the minimum requirements that a bio-packaging prototype must comply to be categorized as suitable and sustainable.

2.2.4 Antioxidants

Demand for agricultural products by 2050 is expected to increase by 50% compared to current levels (Ramírez-Pulido et al., 2021), which is likely to lead to greater amounts of waste and secondary streams. Agricultural waste is the sum of crop losses, material unacceptable for market or consumption, industrial side streams, and food waste from consumers and services (Fritsch et al., 2017). It is estimated that one third of all food produced along the food chain is managed as waste (Bedoić et al., 2019), amounting to more than 1.3 billion tons per year (Gustavsson et al., 2011).

In this sense, significant efforts have been made in the development of food waste and residue valorization strategies with the objective of closing the loop to produce high value-added composites (Sepúlveda et al., 2018). Although the most widespread uses of these secondary streams are animal feed or biofuel production, they could potentially be used as resources for the extraction of bioactive compounds and antioxidants, used as functional and natural additives in the food, cosmetic and pharmaceutical sectors (Akao, 2018).

Vegetables are outstanding sources of bioactive compounds and antioxidants. One of the predominant antioxidant compounds in vegetables, such as beets, are phenolics and betalains. The most abundant phenolic compound in beets is gallic acid, with health benefits including anti-inflammatory, antioxidant and metabolic functions (Baião et al., 2020). However, other compounds may also be present: chlorogenic and syringic acids, quercetin, p-hydroxybenzoic and p-coumaric acids (Singh et al., 2019). As for betalains, their presence in beet is remarkable (Sigwela et al., 2021) and are considered one of the ten most potent natural antioxidants (Carrillo et al., 2017) and the most effective inhibitor of lipid peroxidation (Singh et al., 2019). In addition, betalains also have potent anticancer, antibacterial and anti-inflammatory properties, making them potential bioactive compounds (Fu et al., 2020).

Thermotolerance and thermodynamic stability of these compounds must be taken into account when developing a strategy for the extraction and recovery of antioxidant compounds from beet residues and side streams. Conventional extraction methods, such as Soxhlet and maceration, are widespread; however, environmental awareness has led to the search for new extraction technologies with better environmental profile and efficiency, denoted as “Green Emerging Technologies”(Nirmal et al., 2021).

Despite the interest in the extraction and recovery of bioactive compounds and antioxidants from agricultural residues, most research has been conducted at the laboratory scale. On the other hand, when looking for a new biotechnological route to implement, it is important to demonstrate its technical feasibility, as well as to estimate its environmental burdens, i.e., how this new approach could "help the environment" with

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the recovery and use of these waste streams, whether it could be considered as a sustainability approach and how much the environmental burdens are being reduced.

In this sense, the aim of **Chapter 12** is to perform the process modeling and environmental assessment of the envisioned scale-up process of different methods of antioxidant extraction from beet residues, both leaves and stems, seeking to evaluate which of them is the most efficient and environmentally friendly. In addition, to evaluate the cost-effectiveness of the proposed extraction methods, the operating costs of the whole production process will also be considered.

In the same line as **Chapter 12**, on **Chapter 13** it is developed a biotechnological framework for the valorization of agrifood and forestry related residues for the production of resveratrol using a fermentation step in which the resveratrol is obtained thank to the fermentable sugars available on the residual input streams. Particularly, three-related streams of wine production process have been recovered, vine pruning residues, coming from the agricultural activities, wine lees and grape must, residual side streams produced during the wine production scheme, together with cheese whey, coming from dairy industry, and forestry residues. The aim of this chapter is to develop a large-scale modelling of the facility, considering as production capacity the valorization of 100 ton/batch of residual streams, the environmental assessment of the alternatives, the economic profitability evaluation and also the eco-efficiency analysis, aiming to provide a global evaluation for the selection of the best resveratrol production scenario.

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SECTION II

Comparative evaluation of methodologies to analyze the sustainability of bioprocess scenarios

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SUMMARY

The effective implementation and development of bio-based production systems requires their analysis and evaluation through the use of comprehensive and well-developed impact assessment methodologies. Although the use of bio-based feedstocks and biotechnology-related technologies should be classified as an advantageous sustainable strategy, given the expected reduction in the use of fossil resources and the enhanced recovery of value-added compounds available in bio-related feedstocks, it is necessary to effectively demonstrate that it is indeed as sustainable as expected.

In this regard, the use of quantitative assessment methodologies capable of providing, throughout the development of well-defined procedural steps, impact scores associated with the process under evaluation, related to environmental burdens and economic profitability, two key aspects for a subsequent implementation of a large-scale biorefinery in the "real" market value chain, becomes necessary.

Besides, these assessments should also be used for allowing the comparison between different emerging production models and also among the ones based on the conventional use of fossil resources and linear manufacture. This comparative analysis is suitable to assess the advantages of going through a bio-based process instead of a traditional chemical route, and also to detect improvement needs, since in most cases the lack of optimization of emerging technologies could be a drawback and an impediment to their implementation.

To this end, **Section II** introduces the assessment methodologies that has been further used in the thesis, including the Life Cycle Assessment (LCA), defined and explained in detail in **Chapter 3**, since it is the main assessment methodology used throughout the research studies developed in the thesis, and Planetary Boundaries, whose analytical procedure has been included in **Chapter 4**. On the other hand, it is worth mentioning at this point that another methods has been used in a research report, the G2 Greenness Grid methodology, based on the principles of Green Chemistry, and the eco-efficiency analysis following ISO 14046. However, since it has been combined with the LCA for an in-depth analysis according to the methodological procedure, its definition and main concepts have been added as a complementary section of **Chapter 3**.

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3

Life Cycle Assessment methodology

SUMMARY

When new bio-based processes are developed to provide innovative alternatives that promote the rules of the circular economy, through the valorization of waste streams from agricultural and industrial processes, it is important to carefully evaluate their characteristics in order to compare them with synthetic-based analogues, i.e., those that are widely developed and implemented in the industry, production processes and in the market. In this way, it will be possible to obtain a global vision of their market opportunities, their improvement ranges, potentialities and shortcomings.

When talking about bio-based products, it is important to bear in mind a fundamental aspect: "bio-based products do not necessarily have to be environmentally friendly". There are two concepts that seem to go hand in hand, but in fact are not necessarily linked. While the recovery of waste resources is a plus, as it leads to avoid the depletion of fossil resources and favors the reduction of waste to landfill (for example), the associated processes for the functionalization of raw materials in the formulation of bio-adhesives involve the use of chemical agents and energy, two aspects that can significantly affect the environment. Faced with this issue, the life cycle analysis methodology proves to be an effective tool to evaluate the potentialities of the bio-based manufacturing process with the aim of being in line with a sustainable model.

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3.1 General overview of sustainability assessments

Chapter 1 has introduced the main core of sustainability, built on the basis of the main definition of sustainable development, which aims at enabling and improving the quality of life of social communities but avoiding going beyond the Earth's resources. But, in order to effectively assess how sustainable a scenario is, there is a need to apply appropriate tools to measure as accurately as possible its influence on the stability of the Earth. In fact, the report prepared by UNEP, *Towards a Life Cycle Sustainability Assessments*, describes "the need to develop a methodological framework and the urgency of assessing complex systems that are acknowledged globally".

In this sense, Life Cycle Thinking (LCT) is fully related to sustainability, as it provides a comprehensive assessment of all impacts and consequences associated with the life cycle of a product or process, including economic, environmental and social effects. It is defined as a theoretical approach that quantitatively and qualitatively assesses impacts on the three pillars of sustainability for both products and processes at an early design stage, at a medium/high TRL or in a well-established sector of activity. It is considered as a meaningful, feasible and suitable method for accurate analysis of alternative production scenarios, providing information on potential improvements and identification of key impact contributors. LCT is a framework that aims to provide a holistic approach and is considered a useful tool for assessing the relationships between different sectors. The definition and achievement of objectives and goals is proposed for the entire value chain and as a philosophy of the company (Jacob-Lopes et al., 2021; Moni et al., 2020).

Generally speaking, the main benefits that could be derived from the use of a LCT approach are listed below (Mazzi, 2019):

(1) Promote a comprehensive and accurate analysis of all the components contributing to the impact of a scenario under assessment
(2) Helping to identify alternatives to improve the overall performance of a production model or supply chain management
(3) Provision of comparative analysis of alternative solutions
(4) System-wide improvement with consideration of supporting more sustainable approaches

LCT encompasses three advanced models known as the life cycle assessment (LCA), life cycle costing (LCC) and social-LCA (S-LCA), aiming to assess the three pillars of sustainability. However, the LCA is the unique methodology perfectly described and standardized in the ISO 14040 and ISO 14044, as the LCC and S-LCA are not available in a specific international standard, just in the form of guidelines, as the case of S-LCA, developed by the UNEP and SETAC (Society of Environmental Toxicology and Chemistry) in 2009 (Toniolo et al., 2019).

Given the standardization of the LCA methodology, in this thesis it is the tool that has been applied to study the environmental feasibility of the proposed bio-based scenarios. This development has been approached according to ISO 14040 and ISO 14044, whose main stages and characteristics are defined in the following section.

3.2 Life Cycle Assessment

Life cycle assessment (LCA) is a robust, well-developed and widely use methodology to assess the environmental loads of products and services throughout their life cycle. The first LCA guideline was developed by SETAC, in 1993, and subsequently standardized by ISO 14040 and ISO 14044 in order to provide a more consistent

framework (Hosseini et al., 2023). The most important developments in the definition and development of LCA are described in **Figure 1**.

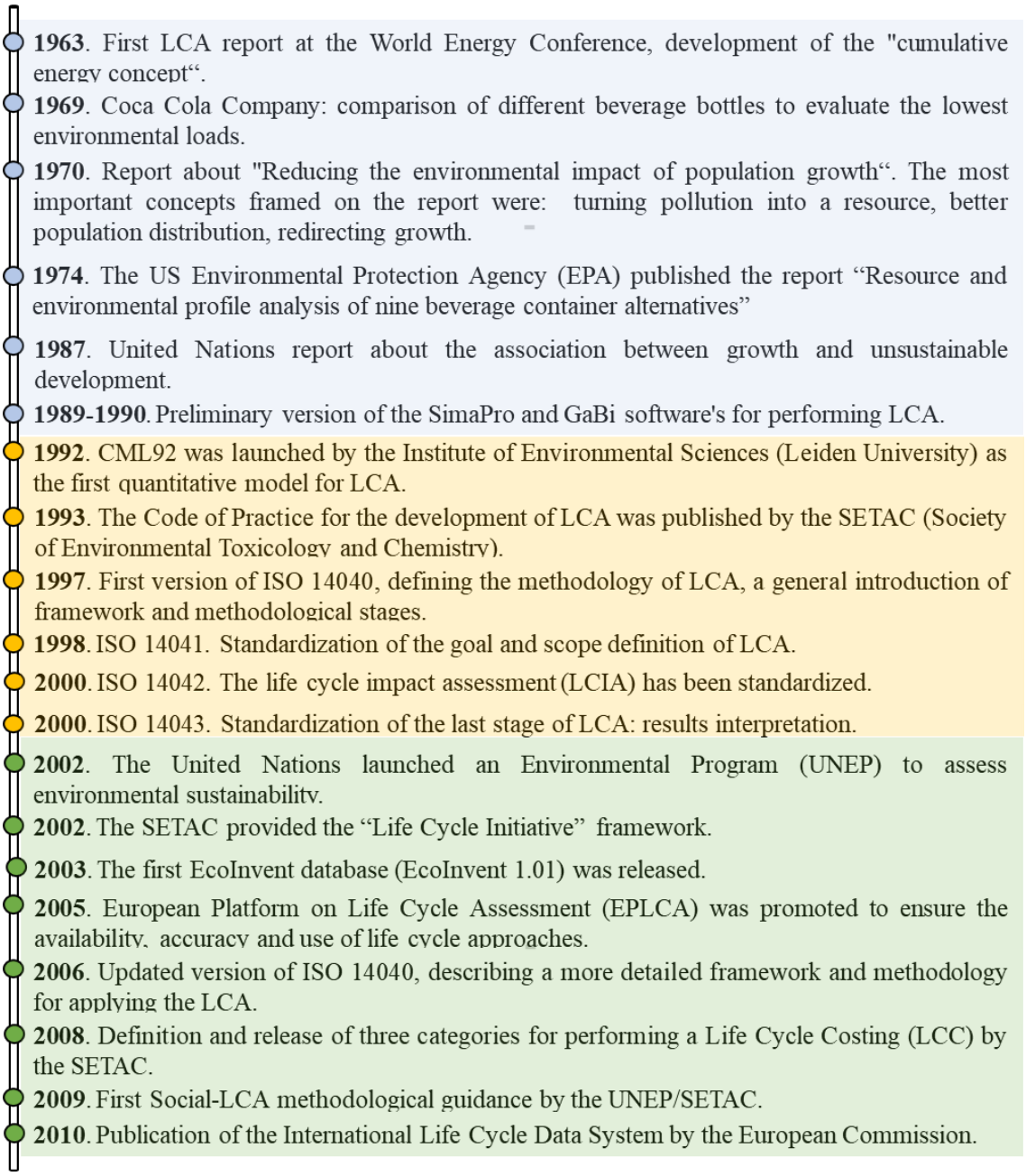

Figure 1. Main achievements in the definition and development of LCA methodology. Color code: blue (Concept definition, early-stage of LCA development), yellow (decade of methodology standardization) and green (period of elaboration of a common agreement and LCA interpretation) Source: Own elaboration.

The use of the LCA methodology provides a benchmark for future research and innovations to provide further environmental sustainability procedures with reduced impact burdens and further achievements in circular economy concepts (Yousaf et al., 2024). It has been pointed out that among the three pillars of sustainability, the environmental dimension is the most important. This assertion has been made based on

the fact that both the economic and social dimensions depend on the Earth's resources (i.e., the quality of the environment), thus directly on the environmental pillar.

The evaluation of a process scenario under an LCA perspective requires the development of four main stages (**Figure 2**), defined in ISO 14040 and ISO 14044, which are described in depth in the following sections.

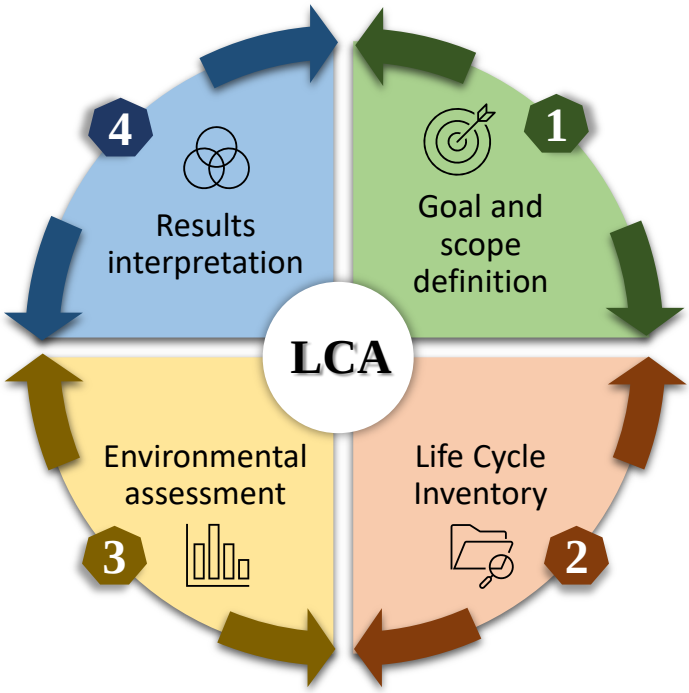

Figure 2. LCA methodology. Main stages. Source: Own elaboration.

3.2.1 Goal and scope definition

The definition of the goal of the assessment aims to identify the purpose of the study, the rationale behind conducting an environmental approach, as well as the future application of results obtained (i.e., for stakeholders, for dissemination to the general public, for policy makers, etc.). A common objective that could be defined when performing an LCA is the assessment of environmental burdens, the identification of the main contributors on the potential impact, as well as the comparison with other alternative configurations and the performance of sensitivity analyses to improve the quality of the scenario under evaluation. On the other hand, identifying the scope of the assessment refers to the areas of application, the dimension of the study, along with the degree of detail of the analysis being performed (Ren and Toniolo, 2019).

The scope of the assessment is directly related to the definition of the system boundaries, which aims to identify which process units and stages are included in the analysis. The description of the system boundaries depends on both the scope of work and the stakeholders and target audience (Caretta et al., 2021). According to ISO guidelines and bibliographic references, there are several alternatives on the definition of the system boundaries, depending on the selected boundaries of the assessment, which are defined in **Table 1**.

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Table 1. Main system boundaries and scopes that could be used when performing an LCA

Approach	Extraction of materials	Production phase	Product(s) transport	Use phase (other facility or consumer)	Post-/waste treatment	Final disposal
Cradle to grave	X	X	X	X	X	X
Cradle to site	X	X	X			
Cradle to gate	X	X				
Gate to gate		X	X	X		
Well to wheel	X	X	X	X		
Gate to grave			X	X	X	X

The most recurrently used approach is the cradle-to-gate, as it is suitable for assessing the adequacy of the production process under a sustainable perspective, where it is easier to identify potential hotspots (those stages with higher environmental impact load) and propose alternative solutions, since the use phase, post-treatment and final disposal stages are not included within the system boundaries (Yang and Rosentrater, 2020). On the other hand, when aiming to assess the entire value chain, including the use phase and the management procedures required for waste streams and final disposal strategies, the cradle-to-grave approach is considered the most appropriate (Moretti et al., 2021).

Industrial symbiosis aims to convert a co-product from one facility into a valuable resource for another, but sometimes the geographical area or transportation requirements lead to significant environmental impacts, higher compared to the management of this stream as waste. In this sense, the use of a gate-to-gate approach is the most useful, as it considers all actions to be taken from the "gate" to the facility 1 to the "gate" of the facility 2, and the results obtained could be used for an early-decision on how to proceed with the output streams: valorize or manage as waste (Ahmad et al., 2020).

Finally, seeking to analyze the impacts derived from the use of the product and its subsequent management, a gate-to-grave approach is presented as the most recommended, as it includes all stages from product transportation to the consumer to its final disposal (Sözer et al., 2020).

On the other hand, other important elements to be defined in this first stage of assessment is the functional unit (FU), defined as the reference score for which all inputs (materials and energy) and outputs (products and co-products, emissions and waste to be treated) of the sub-assessment system are assigned (Yousaf et al., 2024). The rationale behind this is based on the fact that all related and collected data from the process under assessment will be provided referred to the FU.

3.2.2 Life cycle inventory (LCI)

The second step of an LCA is the collection and compilation of all process-related data in order to provide the Life Cycle Inventory (LCI) of the scenario under analysis. The data to be shown in an LCI could be classified into two main groups: inputs from technosphere (including materials, natural resources, chemicals, energy) and outputs to

technosphere (product(s), co-product(s), emissions to air/water/soil, waste to treatment, final flows) (El Joumri et al., 2023). In this regard, the development of mass and energy balances, of an input-output analysis, is required. On the other hand, all the data collected and variables assessed should be based and provided on the FU previously defined on the previous stage (Caretta et al., 2021).

It is important to note that this phase of the LCA is essential for the successful completion of the scenario analysis, as all values subsequently obtained depend directly on the LCI data. For this reason, the time committed for this stage must be extensive, since the data used must be of the highest possible quality (Yang et al., 2019). Sometimes, not all process data are available, either because of lack of information, or because it is not possible to calculate them directly or there is no access to them. Given this the development of modeling and simulation studies is appropriate, as well as recommended since the degree of uncertainty between the actual and estimated value is lower.

At this point in the LCA assessment, the quality of the data and the uncertainty of the LCI should be assessed through a completeness check (to confirm that all necessary data are available and complete), a sensitivity check (to assess the reliability of the database) and a consistency check (seeking to assess whether the assumptions made are consistent with the predefined objective and scope of the study) (Lin et al., 2019; Toniolo et al., 2019).

3.2.3 Environmental assessment

Once the LCI has been constructed, the next step is based on the quantification of all system inputs and outputs within a calculation methodology that uses characterization factors to transform the data into environmental loads, using the following general equation (Eq. 1):

$$EP_{j,i} = Q \cdot EQ_{j,i} \qquad \text{Eq.1}$$

Where $EP_{j,i}$ is the environmental load of the substance i in the impact category j, Q is the amount of substance i in the LCI and $EQ_{j,i}$ referes to the characterization factor in order to "transform" the amount of substance i into an environmental load potential.

The value of EQ depends on the type of characterization model used, there are different calculation methodologies available for the calculation of the associated impact loads. However, among the existing models, the most widely used is ReCiPe, a harmonized model that has been developed based on the CML 2001 and Eco-Indicator 99 methods (Huijbregts et al., 2017). ReCiPe is the preferred method in Europe to perform a LCA, and the most used by researchers to assess the potentiality of a bio-based alternative process in comparison with the synthetic routes (García-Velásquez and van der Meer, 2023). In addition, it is worth mentioning that there are other methods to assess the environmental burdens of bio-based materials, with the Product Environmental Footprint, ReCiPe and IMPACT World+ being the most prominent (Bulle et al., 2019; Turk et al., 2020; WOLF et al., 2010). It provides a total number of 18 midpoint impact categories and endpoint scores, covering the midpoint values into only three categories: Ecosystems Quality, Human Health and Resources (**Figure 3**).

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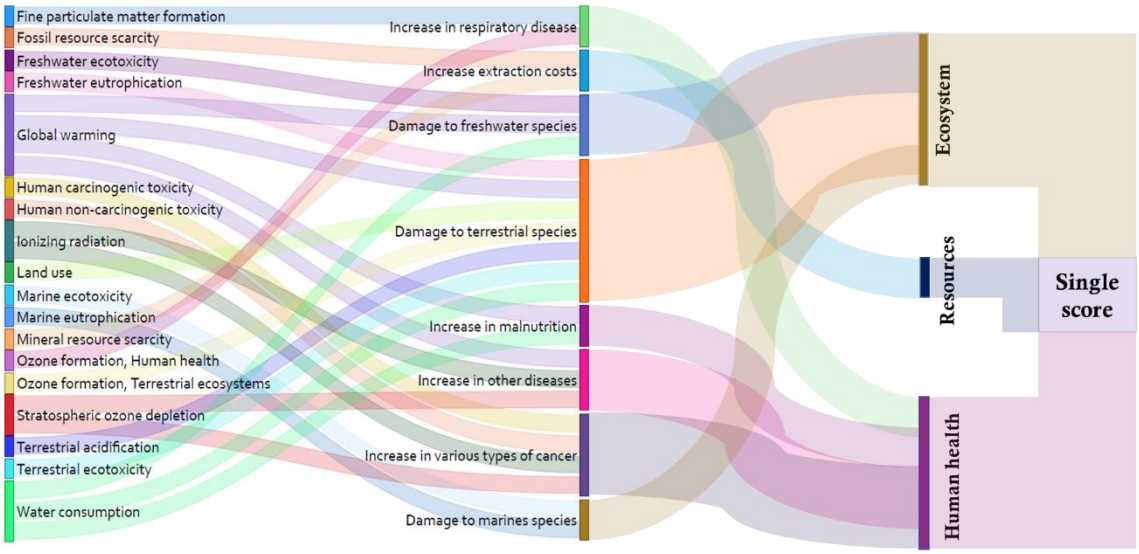

Figure 3. ReCiPe calculation methodology: from midpoint to endpoint. Source: Own elaboration.

3.2.4 Results interpretation

The interpretation and analysis of the environmental scores obtained after the application of the methodology is the last step of the LCA. It is at this stage where the main impact contributors are identified, and also where sensitivity analyses are performed. The main objective of this stage is the evaluation of the environmental burdens, as well as the identification of the strengths and weaknesses of the scenario under evaluation on the scope of sustainability (El Joumri et al., 2023; Yang et al., 2019).

Once the environmental profile of a biorefinery-cascade process has been obtained, it could be interesting to develop an allocation approach to identify the impacts associated with each of the products obtained. In this way it is possible to assess the suitability of a multi-product production, as well as to identify which product or products have the highest impact. In general terms, there are two types of allocation (1) mass allocation, where the impacts are quantified according to the mass ratio between the inputs and outputs of the system and (2) economic allocation, with a procedure analogous to mass allocation, with a procedure analogous to mass allocation, with the difference that in this case it is based on monetary values. In this way it is possible to obtain an accurate relative assessment of the relevance of each of the outputs obtained, both at the level of mass productivity and economic performance (Kyttä et al., 2022; Michiels et al., 2021).

3.3 Greenness Grid (G2) methodology

Seeking a broader analysis for processes under development under the premise of Green Chemistry, the combination of LCA with the Greenness Grid (G2) methodology appears as a suitable approach as it combines the 12 principles of Green Chemistry and integrates the life cycle perspective in standardized quantitative and qualitative models. It is considered as a multidimensional approach focused on the reduction of the use of toxic substances and on process alternatives with the lowest possible waste generation (Reyes et al., 2023).

In fact, regarding the selection of appropriate solvents and chemicals, a categorization has been established to classify the available alternatives from "Recommended", being the least toxic (i.e., water, ethanol, ethyl acetate, etc.), to "Highly

hazardous", which are the most toxic substances, such as chloroform or nitromethane, among others (de Marco et al., 2019; Rosa et al., 2022).

The combination of G2 with the LCA methodology has been considered since, despite the effectiveness of the G2 method, certain aspects related to raw materials or products cannot be assessed in detail using this metric, but with this combination, these shortcomings are met (Saxe et al., 2022).

3.3.1 The basis of the G2 methodology: Green Chemistry

The G2 assessment method is based on the calculation of the "Green Index", a single score obtained by the sum of a total of 15 metrics encompassing the 12 principles of Green Chemistry. Green Chemistry (GC) was first defined in the 1990s as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances" and was further developed and defined when the Institute of Green Chemistry was founded in 1997, leading to the first journal on the subject by the Royal Society of Chemistry in 1999. The rationale behind the GC is based on the concept of "design", providing a total of 12 "design rules" to be followed seeking to achieve sustainability throughout the life cycle of a production process or manufacturing sector (Anastas and Eghbali, 2009; Zimmerman et al., 2020). A summary of the main concepts integrated on the 12 GC principles is represented in **Table 2** (Abdussalam-Mohammed et al., 2020; de Marco et al., 2019; Kennedy and Chapman, 2019; Saleh and Koller, 2018).

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Table 2. 12 principles of Green Chemistry

Principle	Definition
1. Prevention	Enhance the avoidance of producing waste instead on its post-treatment or clean up
2. Atom economy	Efficiency on the reaction routes: "how much initial compounds are incorporated in the final product" (i.e., yield or process efficiency)
3. Less hazardous	Advocation for safer designed reactions and production routes, avoidance the production of hazardous waste
4. Safer chemicals	Process design should be based on the selection of efficient and low toxic chemicals
5. Safer solvents and auxiliaries	The design of process alternatives should be based on using safer compounds with reduced toxicity
6. Energy efficiency	Optimization of the process energy requirements, wherever possible, mild process operational conditions should be used
7. Renewable feedstocks	Promote the use of renewable feedstocks rather than fossil-based, which is availability is limited
8. Reduction of derivatives	Derivatization process should be avoided, as those lead to increased waste and decreased yields
9. Use of catalysts	Catalytic reactions are more quickly and selective, thus reducing waste production and energy demands.
10. Design for degradation	To avoid the production of harmful waste, the process route and chemicals selected should be designed to enhance degradation and avoid environmental persistence
11. Real time analysis	Process monitoring continuously performed to detect and control pollution and other environmental harmful impacts
12. Accident prevention	The design of the process should be based on the aim of minimizing accidents, including emissions, explosions and fires, among others

3.3.2 Putting the G2 methodology into practice

The 12 principles illustrated in **Table 2** are quantified according to a set of equations and procedures defined by the research report of Pinto et al. (2020), which has developed a total of 15 metrics encompassing all the GC principles. A summary of the methodological approach for the application of the methodology, including the main equations, associated with each principle, and other required inputs to be assessed for scoring, is presented in shown in **Table 3**. It should be mentioned that three additional principles are included in order to calculate the Green Index, with the objective of providing a broader and deeper analysis taking into account the actual awareness and targets of the SDGs. The 13th principle is Carbon Efficiency, aiming to represent the C-flow of the process, as it is directly related to the potential carbon footprint and greenhouse effects.

The 14th principle is related to Reaction Efficiency, focused on enhancing the development of less harmful reactions with higher yields and efficiency. The reason behind this principle is the need to include awareness of the integral use of resources and avoid resource depletion.

Lastly, the 15th principle is the Process Productivity, which is in fact directly related to the previous one, with the difference that in this case it is more focused on the ratio between outputs and total inputs, while in the previous one it is between outputs and chemicals.

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Table 3. Metrics for the scoring of the GC principles (Source: Own elaboration based on (Pinto et al., 2020))

Principle	Metric	Definition
1. Prevention	$E_{factor}= \frac{m_w}{m_p}$	m_w is the mass of waste (kg) and m_p the mass of products (kg)
2. Atom economy	$A_e= \frac{Mm_p}{Mm_r} \cdot 100$	A_e is the atom economy (%), Mm_p the molar weight of products (kg) and Mm_r the molar weight of reactants (kg)
3. Less hazardous	$HI= \frac{HTI + ETI}{2}$	HI is the hazard index, HTI the human toxicity index and the ETI the environment toxicity index
4. Safer chemicals	$HI= \frac{HTI + ETI}{2}$	HI is the hazard index, HTI the human toxicity index and the ETI the environment toxicity index
5. Safer solvents and auxiliaries	$HI_T= \sum (SHI \cdot \frac{m_s}{m_{i,s}})$	HI_T is the total hazard index, SHI is the hazard index of the substance m_s is the mass of substances (kg) and $m_{i,s}$ the mass of assessed substance (kg)
6. Energy efficiency	$EI= \frac{ECI + EnCI}{2}$	EI is the energy index, ECI the economic cost index and EnCI the environmental cost index
7. Renewable feedstocks	$F = \sum (\frac{m_i \cdot SF}{m_{i,T}})$	F is feedstock, m_i is the mass of input (kg), SF the sustainability factor and $m_{i,T}$ is the total mass of inputs (kg)
8. Reduction of derivatives	$D = \frac{m_d}{m_p}$	D is the derivatives metric, m_d the mass of derivatives (kg) and m_p the mass of products (kg)
9. Use of catalysts	$C = CU \cdot Y$	C is the catalyst metric, CU the catalyst usage and Y the reaction yield
10. Design for degradation	HLI = 1- I(HL, 1.00, 2.41)	HLI is the half-life index and HL the half-life. * Exponential
11. Real time analysis	$HI_T= \sum (SHI \cdot \frac{m_s}{m_{i,s}})$	HI_T is the total hazard index, SHI is the hazard index of the substance m_s is the mass of substances (kg) and $m_{i,s}$ the mass of assessed substance (kg)
12. Accident prevention	$APP = \frac{\sum (APS)}{n_s} + API$	APP is the Accident Prevention, APS is Accident Prevention Substances, m_i is the number of substances and API the Accident Prevention of Interactions
* 13. Carbon efficiency	$C_e= \frac{C_p}{C_r} \cdot 100$	C_e is the carbon efficiency (%), C_p is the carbon mol in products (kg) and C_r the carbon mol in reagents (kg)
* 14. Reaction efficiency	$R_e= \frac{m_p}{m_r}$	R_e is the process productivity (%), m_p is the mass of products (kg) and m_r the mass of reagents (kg)
* 15. Process productivity	$P_p= \frac{m_p}{m_i}$	P is the process productivity (%), m_p is the mass of products (kg) and m_i the mass of inputs (kg)

In this way, using the guidelines in **Table 3**, a single final score is obtained, known as the Green Index, whose value could be in the range of 0 to 15, with 0 being the worst result, representing an unsustainable process, and 15, the ideal value, indicative of a sustainable model. In addition, a color code could be used to qualitatively represent the value of the Green Index obtained after the development of the G2 methodology (**Figure 4**).

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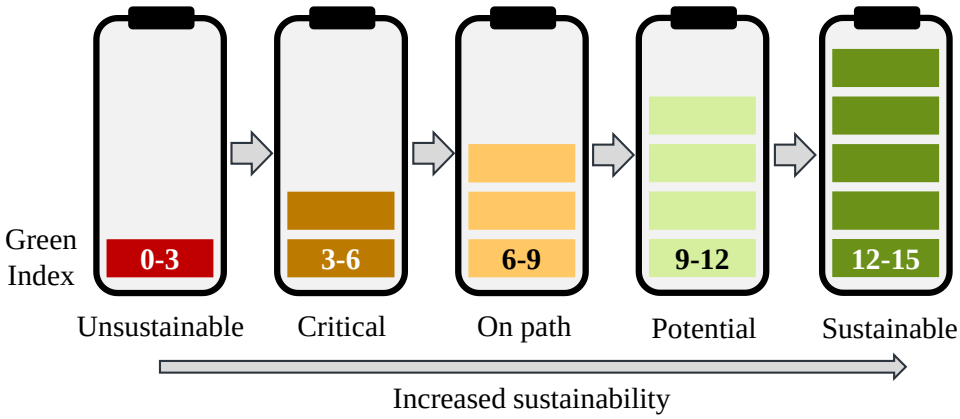

Figure 4. Color code and Green Index categories considered in the application of G2 methodology. Source: Own elaboration.

3.4 Eco-efficiency analysis

The first instance of an eco-efficiency assessment was introduced by the BASF company, as a tool to simplify and easily reach a decision on driving industrial products towards sustainable procedures, as this assessment enables to harmonizes two pillars of sustainability: economic and environmental (Grosse-Sommer et al., 2020). This encompass could be considered as an effective manner to select the best alternative from a sustainable perspective, as sometimes one alternative is more suitable from an environmental point of view, given its lower impact values per category, but on the other hand, it is not economically viable, usually because the costs associated with production are higher than the benefits that can be obtained from the sale of the product obtained (Caiado et al., 2017; Peças et al., 2019; Sengupta et al., 2015). This is the reason for which this integration is useful to overcome these screening issues since, through a series of ratios, it indicates which alternative is the most eco-efficient through the combination of economic and environmental values.

In order to evaluate some of the bio-based scenarios presented in this thesis, three eco-efficiency indexes were used, where not only economic and environmental aspects were taken into account, but also production considerations. The ratios used have been the following, all of them referring to the environmental loads obtained from the implementation of the LCA methodology: production costs, revenues/minimum product selling price and production capacity.

With respect to the first eco-efficient ratio, that of costs against environmental loads, those scenarios that have a lower associated production cost and a lower environmental impact will be those categorized as eco-efficient, while the process alternatives that achieve a higher volume of revenues or a lower minimum product selling price to be economically viable (second assessed ratio), as well as a higher production capacity (third measured ratio), are also the most eco-efficient ones.

On the other hand, it is important to mention that the results obtained are presented in the form of a figure, in which four regions are depicted: a green region, which is classified as the eco-efficient one, a red region, the non-eco-efficient, and two yellow regions, which refer to intermediate situations between an eco and a non-eco-efficient scenario.

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Thesis roadmaps and objectives

The objective of this doctoral thesis is to evaluate the potentiality of bio-based production schemes by quantifying the environmental advantages and drawbacks following a life cycle perspective. The document is structured in seven sections, each of them sub-divided into chapters, as depicted in **Figure 5**.

Section I. Introduction. The goal of this section is to provide a state of the art of sustainability principles related to biorefinery and biotechnology approaches, including also bio-based products that could be obtained through the development of these production models. For this purpose, **Chapter 1** is based on a first approach on what is the basis of sustainable and circular economy and what is the role of bio-based facilities on the way to sustainability. While this first chapter is an overview of the trends and objectives of sustainable development, **Chapter 2** provides a more focused view on how the valorization of waste streams should be realized with the aim of producing bio-based products with high added value. This second chapter includes the identification of the main input "waste" streams that have been used for the assessments developed throughout the thesis, together with a brief discussion of their valorization alternatives.

Section II. Benchmarking methodologies to analyze bioprocess scenarios. This section aims to introduce the main principles of the methodological tools applied in the following sections. Basically, life cycle assessment is the main methodology used throughout the thesis, but also two additional methods have been assessed: the G2 greenness grid and the planetary boundaries. The rationale behind the additional use of the aforementioned methodologies is to introduce the concept of “Green Chemistry”, by the G2 greenness grid tool, and to go beyond the narrower focus of analysis provided by LCA to reflect the environmental effects in a broader expansion, towards planetary boundaries. The section is divided into two chapters, **Chapter 3**, focused on the definition of the main stages of the LCA methodology, including also the description of the G2 tool, and **Chapter 4**, centered on the description of the assessment within a planetary boundary approach.

Section III. Formaldehyde-free bio-adhesives for wood-based panels. The focus of this section is the provision of alternative adhesives for wood-based panels to replace formaldehyde, a compound harmful to environmental and human health. In this regard, various bio-based resources are analyzed as raw materials for the production of formaldehyde-free bioadhesives, with the objective of identifying the suitability of each of them and establishing comparative scenarios with the aim of selecting the best substitute. To this end, **Chapter 5** includes the development of lignocellulosic-based adhesives, considering as feedstocks both Organosolv and kraft lignins. **Chapter 6** covers agri-food related alternatives for the production of bioadhesives, including tannins, soybean and starch. On the other hand, for all case studies, a comparison with conventional formaldehyde-based adhesives is also discussed, with the aim of detecting the main advantages and disadvantages from an environmental point of view.

One of the main thresholds of the LCA methodology is the definition of system boundaries when it comes to assessing the impact of a process or production on a global scale. The boundaries define "where" the study is done, which avoids the ability to analyze the effects of the "unbounded" scenario. This gap could be avoided through the application of the planetary boundary methodology, which is introduced in **Chapter 4** and applied in **Chapter 7**, where the impact of the bio-adhesive alternatives developed in **Chapter 5** and **Chapter 6** are studied on a global scope.

Section IV. Antimicrobials from agro-industrial by-products. The main objective of this section is the valorization of agro-industrial by-products for the production of

nisin, an antimicrobial with proven beneficial properties for both human health and food preservation. Its traditional manufacture involves high-cost inputs, which makes it an unfeasible production scheme. In this sense, **Chapter 8** considers an alternative procedure using food-related wastes, specifically sugar beet pulp, corn stover and cheese whey are the main raw materials studied to produce nisin. On the other hand, seeking to provide a broader alternative scheme, agricultural and forestry residues are also analyzed as bio-based inputs, specifically eucalyptus residues and olive pruning, which are analyzed in **Chapter 9**.

Section V. Active food bio-films from lignocellulosic waste valorization. The purpose of this section is divided into two main chapters. In **Chapter 10**, the objective is to provide a biotechnological production model to obtain polylactic acid (PLA), using wheat straw as feedstock. Furthermore, in order to offer a bioproduct with higher added value, the possibility of using this PLA as bio-based food packaging is evaluated, using nisin as food preservative. Furthermore, seeking the provision of a methodological approach with the objective of identifying the potentiality of an early design food packaging alternative, a multi-criteria roadmap is developed in **Chapter 11**, based on the definition of the basic requirements to achieve a sustainable and circular prototype.

Section VI. Antioxidants. This section aims to perform the modeling of the expected scale-up process of different methods of antioxidant extraction from beet residues, both leaves and stems, seeking to evaluate which of them is the most efficient in terms of yield and more environmentally friendly. Both conventional and emerging green extraction technologies are analyzed, seeking to provide a crude number of alternatives for the valorization of agri-food related waste streams for the recovery of bioactive compounds, such as antioxidants. In this context, **Chapter 12** is developed based on the process modelling of a large-scale bioprocess and the subsequent environmental assessment in order to select the most suitable extraction model. While **Chapter 13** presents three different valorization scenarios of wine-related side streams (vine pruning residues, wine lees, grape must), eucalyptus residues and cheese whey) for the production of resveratrol by the development of a biotechnological process including a fermentation stage.

Section VII. General findings and conclusions. Finally, the last section comprises the summary of the main findings, results and conclusions of the thesis dissertation.

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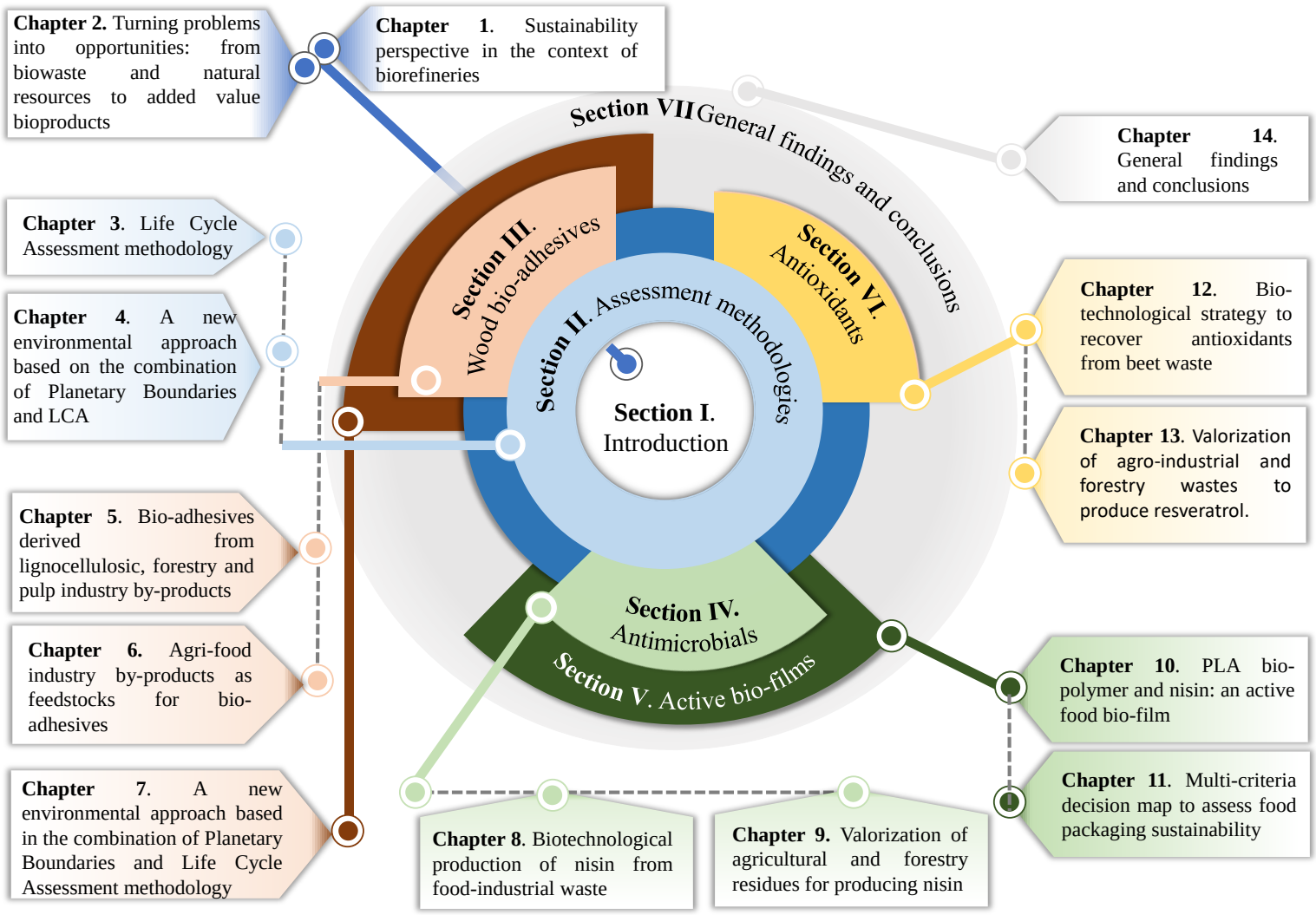

Figure 6. Outline of the structure of the thesis.

4

A new environmental approach based on the combination of Planetary Boundaries and Life Cycle Assessment

SUMMARY

Technological advances, resource availability and the economic development of countries have led to an exponential increase in consumption, population growth and market competitiveness. The integration of new actors in the value chains, from small producers to the end of life of products or processes, has led to the interrelation between the productive sectors, consumers and waste managers. However, the tendency towards the linearity of processes, the habit of "use and throw away", the exorbitant use of resources to satisfy society's demand, as well as social pressures based on unnecessary consumerism, have caused today's society to live beyond the limits of planetary stability. The implementation of policies focused on the reduction of greenhouse gas emissions and the use of bioproducts, as well as interregional agreements that establish climate impact reduction goals, is a fact that represents the importance of being aware of both the use of resources and the emissions involved in their production processes.

In this approach, the use of methodologies for the integral evaluation of productive systems are considered an essential element to assess their adequacy in the market chain, both from the point of view of their involvement in climate change and other environmental burdens that also affect the sustainability and preservation of the planet, such as resource depletion, terrestrial ecotoxicity or eutrophication of the aquatic environment, among others. Therefore, this chapter focuses on the definition of planetary boundaries, how they should be addressed, as well as the methodology for the conversion of environmental loads obtained through an LCA study to global impact values.

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OUTLINE

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4.1 Going further LCA to a global scope

The 21st century can be considered as the century of acceptance that the planet's resources are not limited, of innovation for the development of new processes that use waste as resources, promoting productive circularity, of political and interregional involvement in taking measures to mitigate change, and of a downward trend in society's consumption patterns, as a consequence of economic problems arising from consecutive crises (COVID pandemic, Russia-Ukraine war, terrorism, etc.).

Murphy et al. (2021) have developed an interest report about how the transition to a modern society, based on the unlimited and uncontrolled consumption, is affecting over the compatibility of the planetary limits (Murphy et al., 2021). Both the policy makers, stakeholders and society should be aware of the limitation on the consumption of resources to respond to the society needs and demands but without compromising the stability, quality and capacity of the Earth system. A successful future should bear in mind that growth is limited, that all the actions within the value chains should be analyzed and restricted according to the requirements of sustainable development, and that more efforts and thresholds should be placed when assessing the environmental, technical, societal and economic issues of a product or process under-development.

The challenge on preventing the increased environmental deterioration should be solved by the implementation of policies, economic systems and specific goals encouraging and having an effective impact over the control on growth, good and services productivity and exploitation of natural resources. In this regard, to be aware on the compliance with those implementations, the development of environmental assessments within a planetary scope is necessary.

The concept of planetary boundaries (PBs) offers a framework to evaluate and estimate the capacity of the earth to withstand the effects of the human related production, consumption and economic activities, in the form of environmental loads, over its nature and stability. In the last decade this approach has been an active topic of research by several authors, including the reports on both developing the methodology, the application to different sectors and scenarios and also assessment on how to organize and design supply chains to be in line with the PBs framework (Anders Bjørn et al., 2020a, 2020b; Bunsen et al., 2021; Castellani et al., 2016; Chandrakumar and McLaren, 2018; Cole et al., 2014; Gleeson et al., 2020; Wheeler et al., 2021). One of the main issues when trying to apply the PBs is how to downscale the PBs scores, which implies a systematic translation into boundaries at a lower scale (Guinée et al., 2022).

The PBs actually available to be interrelated with the LCA methodology are divided into nine environmental constraints for production and economic activities to act within (Schenker et al., 2022). Those targets and constrains are mainly defined on the alignment of the Paris Agreement, in which it has been committed to avoid the raising of the global temperature in a value below 2 ºC (Moshrefi et al., 2022). Its aim is to define a delimitation for all the sectors and activities that could entail an impact over the environment in order to be in a “safe operating space (SoS)” for both the planet and the social community (Owsianiak et al., 2022).

This concept of SoS was first defined by Rockström et al. (2009) and afterwards more developed by Steffen et al. (2015) (Rockström et al., 2009; Steffen et al., 2015). In this last report, the methodological definition and evaluation of the PBs related with climate change, stratospheric ozone depletion and ocean acidification have been categorized as being the most detrimental on the maintenance of Earth’s health: “these three impact categories might push the Earth into a new state if crossed, also having a pervasive influence on the remaining boundaries” (Steffen et al., 2015).

On the other hand, it should be taken into account that the complexity of the Earth natural cycles and processes entails a difficulty when trying to establish an accurate threshold for the definition of the PBs values. But, at the same time the capacity of evaluating the scenarios in a lower scale level but under a global scope is essential for going through the best decision on the use of resources, its management, the related emissions expected and to define how to provide a balance between economic growth and environmental maintenance (Bjørn et al., 2019). To this end, control variables are used to categorized and to score the PBs, considered as the "distance from the predicted intrinsic threshold level regarded as safe" (Bergmark and Zachrisson, 2022).

When trying to find an absolute environmental sustainability, it could be achieved by the integration of the LCA with the PBs methodology (Sala et al., 2020; Zeug et al., 2021). It is defined as the assessment of the environmental performance of an anthropogenic ecosystem in terms of its assigned environmental carrying capacities, and it is assessed by using environmental steady-state models (Ryberg et al., 2021; Wowra et al., 2022), looking to determine if the product/process/sector under assessment does not exceed its assigned SoS for any PBs category (Bjørn et al., 2020). Those carrying capacities were recently defined as "the maximum impact that the environmental ecosystem is able to sustain without suffering and affecting over the integrity and functionality of the natural system" (Bjorn et al., 2020).

According to Bjorn et al. (2020), two main approaches could be developed when assessing a scenario under a PB framework: (1) development of a new methodology of "LCA" including environmental indicators within the scope of the PBs and (2) use of the LCA assessment method as it is but, ones applied, integrate the carrying capacities under a global level, thus going further an "static" LCA to a "dynamic and broader" sustainability assessment. The scope followed in this thesis is the second one, as it is considered as a more established and adequate mechanisms within the global framework, as deeply developed characterization models are yet available for the traditional LCA, with defined guidelines and easier to interpretate in comparison to a new methodology.

The main issue in this regard is on the correct definition and scoring of the carrying capacities. In this manner, bibliographic references and advanced research reports are used to its definition and subsequent applied to the LCA values (A. Bjørn et al., 2020; Ryberg et al., 2016; Wowra et al., 2022).

Besides, when assessing sustainability, two main concepts are arisen: relative sustainability and absolute sustainability. Both LCA and PBs assessment are framed within the absolute sustainability concept, as it is developed in the framework that considers the natural tolerance of the environment as limit to assess the potential impact load over it. If a process or scenario under assessment goes beyond the tolerance limit of the environment, then the assessment methodology should be aware on it and it may promote the definition of alternative or improvement "actions" to be applied with the aim of reducing the detrimental impact over the environment (Sanyé-Mengual and Sala, 2022). In this concept of absolute sustainability also the European Green Deal and the SDGs are framed, to this end, a direct relation between PBs and sustainable developed is observed (Sanyé-Mengual and Sala, 2022).

In this context, this **Chapter 4** is based on how to assess the environmental loads within a planetary level, following an appropriate methodology to streamline the characterization values of LCA into planetary boundary (PB) scores, for which a pre-stablished threshold has been identified. This scope is though to provide to researchers, stakeholders, policy makers and practitioners the extent of how a product, a process or an economic sector could interfere over the ecosystem, and also on where to focus for the improvement its overall performance under a PBs perspective.

4.2 Methodology

The integration of LCA and PBs requires a first environmental assessment following the LCA methodology in order to obtain the loads over the impact categories based on the Environmental Footprint/ILCD guidelines (European Commission, 2010; Finkbeiner, 2014; ISO, 2006). This methodology is developed bearing in mind the approach of global sustainability policies, which framework has been firstly analyzed by Rockström et al., 2009 (Rockström et al., 2009). In order to transform the LCA scores, it is necessary to consider characterization factors, that are going to be applied to the inventory items available once the impact scores have been calculated, as only some substances apply for the specific PBs results 13. The next step is transforming the given characterized results for a planetary study level, for which allocation approaches and criteria are needed.

To provide a more effective understanding of the methodological procedure, **Figure 6** is displayed.

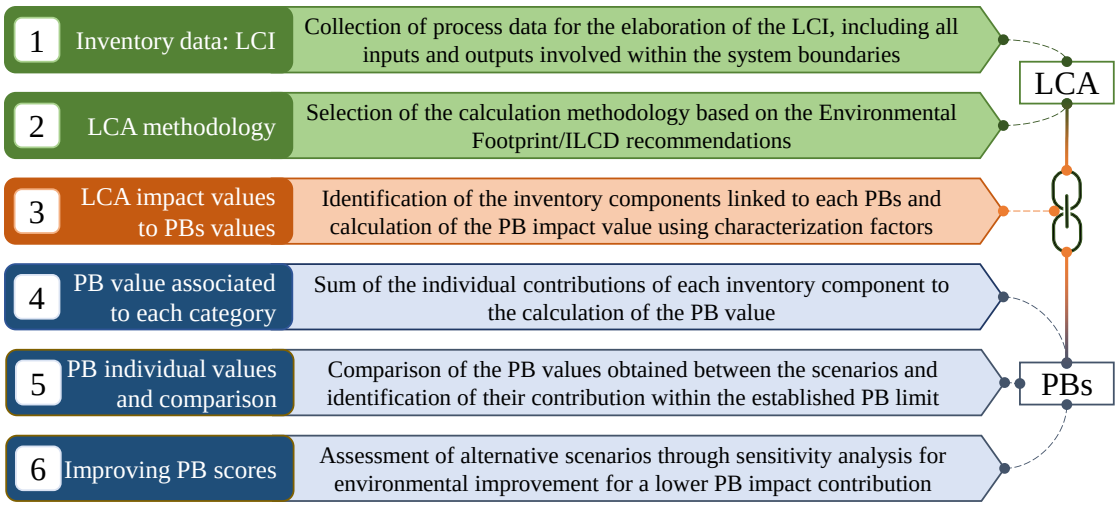

Figure 6. Methodological procedure for assessing the planetary boundaries from the impact values of LCA. Source: Own elaboration.

The first three steps (step 01, 02 and 03) are integrated within the classical LCA methodology, bearing in mind that the selection of the methodology of calculation is based on the Environmental Footprint/ILCD recommendations (as shown in **Table 4**).

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Table 4. Environmental impact categories and their corresponding assessment methodologies according to the Environmental Footprint/ILCD recommendations

LCA impact category	Unit	Recommended method
Climate Change (CC)	kg CO_2 eq	IPCC 2021 GWP100 V1.00
Stratospheric Ozone Depletion (SOD)	kg CFC11	EDIP 2003 V1.03
Eutrophication, freshwater (EF)	kg P eq	ReCiPe 2016 Midpoint (H) V1.06 / World (2010) H
Eutrophication, marine (EM)	kg N eq	
Photochemical Ozone Depletion (POD)	kg CFC11	

4.2.1 Selection of the planetary boundaries under assessment

When the LCA scores are obtained, characterization factors are applied in order to obtain the PBs values per impact category (Doka, 2016). In this regard, the PBs selected for the analysis are the ones presented in **Table 5**, based on the bibliographic availability of the characterization factors necessary to transform the LCA scores into PB_s values.

Table 5. Correlation between LCA impact categories and PBs, including the unit of measurement and the acronyms selected for each one

LCA impact category	PB	Unit	Acronym
Climate Change (CC)	CC- energy imbalance at the top-of-atmosphere	W/m^2	$PB_{CC,imb}$
	CC-atmospheric CO_2 concentration	ppm	$PB_{CC,CO2}$
	Ocean Acidification	Ω_{arag}	PB_{OA}
Stratospheric Ozone Depletion (SOD)	Stratospheric Ozone Depletion	DU	PB_{SOD}
Freshwater Eutrophication (EF)	Biogeochemical flows- phosphorous	Tg P	$PB_{BF,P}$
Marine Eutrophication (ME)	Biogeochemical flows- nitrogen	Tg N	$PB_{BF,N}$
Photochemical Ozone Depletion (POD)	Atmospheric Aerosol Loading	AOD	PB_{AAL}

One of the main drawbacks when evaluating the PBs relies on the variation of the unit of measurement related with the same LCA impact category, as it is the case of CC. While the LCA score only in kg CO_2 eq, for the PBs, three different variables: energy imbalance at the top-of-atmosphere, atmospheric CO_2 concentration and ocean acidification. The energy imbalance score could be categorized as a more inclusive and fundamental variable of control when analyzing the sustainability potential of a region. This variable evaluates how the anthropogenic activities implies variation in the radiative forcing, considering carbon dioxide emissions, greenhouse gases, oxides (both sulfur and nitrogen), organic carbon, ammonia, etc (Pidcock et al., 2021; Sabine, n.d.; Sutton, 2018; Zhongming et al., 2021). This assessment provides a wider vision on the influence of human activities over the global warming potential, rather than only being focused on the

CO_2 emissions. In fact, according to the IPCC report on Climate Change 2021, it has been affirmed that even though the CO_2 emissions are the ones with a more notable contribution over the global warming, the sum of volatile organic compounds (VOCs), nitrogen oxides, halogenates, and methane implies a contribution analogous to that of CO_2 (Zhongming et al., 2021). To this end, it is demonstrated the need to incorporate the impact of the energy imbalance in the upper atmosphere when assessing the planetary boundaries and the sustainability indexes potential.

Regarding the ocean acidification variable, it attempts to focus on the interrelationship and environmental contribution established between emissions associated with climate change and the increase in ocean acidity. This approach includes emissions of nitrogen oxides and sulfur, which, concentrated in the layers of the atmosphere as a result of their emission into the air, return to the terrestrial environment through precipitation, which implies acidification of the environment, both terrestrial and aquatic. One of the ways of measuring this effect is through the measurement of H^+ cations at the ocean surface (Sabine, n.d.). The presence of these cations directly affects the carbon cycle, specifically that of the calcium carbonate compound, expressed in aragonites units, as it is the most soluble form of the $Ca(CO_3)$. This is the rationale behind the use of Ω_{arag} for measuring the ocean acidification PB (Barker et al., 2018; Mass et al., 2017; Zheng and Cao, 2014).

With respect to SOD category, the importance of its assessment relies on the current damage of the ozone layer, that has reached almost 25 million km^2 in 2021 according to the European Environment Agency, affecting over the increase of Earth temperature and implications over human health. This category encompasses the emissions related with GHGs, chlorofluorinated carbonates, CFC and halons, harmful compounds that could be found in the atmosphere and that also affects over the climate change potential ("Agencia Europea de Medio Ambiente — Agencia Europea de Medio Ambiente," n.d.; Health Organization Regional Office for Europe, n.d.).

Regarding the PBs associated with biogeochemical flows, both $P_{BBF,P}$ and $P_{BBF,N}$, relies on the evaluation of the flows of nitrogen and phosphorous between the environment and the living organisms (Guignard et al., 2017; Nesme et al., 2018). Given the importance of preserving a proper balance on the concentration of these compounds, due to their involvement in the maintenance of the natural cycles of living organisms, their consideration on the definition and assessment of planetary boundaries becomes essential. The limits established are based on the values of N and P necessary to maintain, at least, a balanced concentration that allows the maintenance of biogeochemical cycles without a significant alteration on the metabolism of living organisms.

One of the most recognized and essential biogeochemical flows is the one of N_2, developed under a three-stages process: ammonification, nitrification and denitrification (Prangnell et al., 2019; Sadhukhan et al., 2022). The alteration of this cycle could entail a critical issue over the environment, as nitrogen compounds are the primary nutrients for microbial growth. The combustion of fossil fuels, the extensive use of fertilizers in the primary sector and the uncontrolled emissions containing nitrogen compounds are the main contributors, causing an imbalance of nutrients on the soil that could entail an important loss of biodiversity (Bernhard, 2010). A similar argument is given for the relevance of the phosphorus cycle, since it is a compound that plays an important role in energy transfer processes, in the structure of the genetic material, as well as in the composition of cell membranes (Yuan et al., 2018). The activities that have a direct influence over its natural cycle are agricultural harvesting and fertilization, manure, mining activities and animal wastes (Hou et al., 2018; Powers et al., 2016; Yuan et al., 2018).

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Lastly, with the PB related with atmospheric aerosol loading, P_{AAL}, the aim is to evaluate the damage potential of the presence of aerosol particles in the atmosphere, which have an impact on both earth's climate and human health. The interaction of these particles with the water molecules in the atmosphere affects over the water cycles and atmospheric circulation (Lee et al., 2019; Pérez-Díaz et al., 2017; Schepanski, 2018), as well as over other reactions that take place in the atmospheric layers, which are closely related to global warming, given their impact on the reflection and/or absorption of solar radiation (Emetere et al., 2019; Huang and Ding, 2021; Johansson et al., 2012; Zhang, 2020). The monitoring and control of aerosol emissions would imply a further step towards environmental sustainability and the maintenance of human health, therefore their evaluation under planetary limits is considered equally important (Ren-Jian et al., 2012).

4.2.2 Top-Bottom Approach: Downscaling Planetary Boundaries

These PBs scores are assessed under various types of allocation to evaluate if the values are set under the SoS (Safe Operating Space) thresholds, defined as the "operational budget that an anthropogenic activity must not exceed to ensure maintenance within environmentally sustainable global values". In this manner, it is easier to assess the potentiality of products and process to be categorized as sustainable, bearing in mind that the scaling could entail that, for a level of study the scenario under assessment could be sustainable, but when increasing or diminishing the level, the opposite could happen.

These SoS values are calculated as the difference between the planetary limited value (i.e. in the case of the PB related to climate change imbalance ($PB_{CC,imb}$), it is stablished as 350 ppm) and the natural background level, defined as the impact loads scores not including the incidence of human activities (for the case of $PB_{CC,imb}$ is 278 ppm), resulting to a score that falls to 72 ppm, denoted as the "full SoS (SoSf)". In this regard, the definition of both the SoS and SoSf values for the selected PBs impact categories is shown in **Table 6**.

Table 6. SoS, natural background levels and SoS_f for the categories of PBs

PBs	SoS	Natural background level	SoSf
$PB_{CC,imb}$	1 W/m^2	-	1 W/m^2
$PB_{CC,CO2}$	350 ppm	272 ppm	72 ppm
PB_{OA}	2.75 Ω_{arag}	2.07 Ω_{arag}	0.68 Ω_{arag}
PB_{SOD}	275 DU	260 DU	15 DU
$PB_{BF,P}$	11 Tg P	4.8 Tg P	6.2 Tg P
$PB_{BF,N}$	62 Tg N	55.8 Tg N	6.2 Tg N
PB_{AAL}	0.25 AOD	0.14 AOD	0.11 AOD

There is not a common agreement on how to evaluate the allocation shares for each of the scenarios under a planetary level approach. To this end, four different allocation methods has been evaluated: two based on economic, one over the population amount and the last one about the GHG emissions of each regional sector. In this manner, the three pillars of sustainability are being assessed: environmental, through the evaluation

under the GHG emissions perspective, economic, using the data of the gross value added (GVA) and the final consumption expenditure (FCE) and social, with the population census (POP) of each region.

Encompassing the allocation approaches, three different principles could be found, which have been selected as the most useful in previous environmental reports: egalitarian, utilitarian and grandfathering (Hjalsted et al., 2021; Lucas et al., 2020; Meyer and Roser, 2006). In this case, a combination of egalitarian and utilitarian principles has been considered, given the intercorrelation between economic pillar with the social one (FCE + GVA + POP).

The egalitarian principle is based on the premise that environmental burdens should be distributed equitably among the population, whereby the number of inhabitants at the global, European, and national levels will be used as the allocation share factor for calculating aSoS. This principle is also known as the "equal per capita basis", defined as the aSoS allocated on an individual basis in a specific period of time (Perdomo Echenique et al., 2022). In the case of the utilitarian principle, it considers that it would be ideal to establish the necessary guidelines to maximize the welfare of the population, which is why this principle uses the economic parameters of GVA and FCE, as those represent the economic value generated by producers in an economic sector and the level of economic expenditure of consumers, respectively (Weidema and Brandão, 2015).

Finally, the principle of allocation of grandfathering argues that the aSoS should be assessed according to the degree of environmental impact derived from the sector production capacity for a given productive year (Damon et al., 2020). To evaluate the damage factor, GHG emissions were considered as this is one of the most widely used indicators to assess impacts at industrial and sectoral levels as well as it has an extensive database available (European Environment Agency, n.d.).

In this regard, when the PB values are obtained, those are downscaled from the global level to the continental/regional level, considering the sharing of the environmental burdens based on the allocation procedures and using the equations provided in **Table 7**, thus obtaining the assigned SoS (aSoS) to the level under assessment.

Table 7. Equations used for calculating the aSoS scores categorized by the allocation principles.

Allocation principle		Acronym	Upscale	Equation
Combined egalitarian with utilitarian principles	GVA	$aSoS_{GVA}$	R/C[1]	$\frac{POP_{R/C}}{POP_{World}} \cdot \frac{GVA_S}{GVA_{R/C}}$
	FCE	$aSoS_{FCE,\ ind+POP}$	S[1]+POP[1]	$\frac{POP_{R/C}}{POP_{World}} \cdot \frac{FCE_S}{FCE_{R/C}}$
		$aSoS_{FCE,\ ind+POP+VC}$	S[1]+POP[1]+VC[1,2]	$aSOS_{FCE_{ind+POP}} \cdot \frac{VC_{PP\ R/C}}{VC_S}$
Grandfathering	GHG	$aSoS_{GF}$	R/C[1]	$\frac{POP_{R/C}}{POP_{World}} \cdot \frac{GHG_{S,R/C}}{GHG_{R/C}}$

1. The acronym POP refers to the population value at global, regional or country levels. R/C to regional or country level, S to the specific economic sector and VC to Value Chain

2. The term Value Chain (VC) represents the contribution of the production volume or the region or country in the specific economic sector, within the same location. For instance, to its calculation, sector database is considered. To calculate the VC PP, R/C, the production volume of the specific sector for each region is compiled.

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4.2.3 Assessment of the values of aSoS within the sustainability concept

One of the main objectives in the calculation of environmental shares using the allocation principles is to determine the degree of environmental sustainability of the scenarios under assessment, denoted as R_{ES}. It is measured as the ratio between the PB-LCA value calculated for each of the planetary boundaries and the scenarios under evaluation, and the $aSoS_{pp}$, where pp is the type of allocation and the principle used for its calculation. To calculate it, it must be followed the procedure depicted in **Figure 7**: from the PBs scores, calculation of the $aSoS_f$, considering the principles and allocation procedures, to the final result of the R_{ES}. The value of this ratio will be indicative of the degree of sustainability of the production scenario. Thus, if the R_{ES} score is equal to or less than 1, then the scenario is considered as environmentally sustainable, while if it is greater than 1, it means that the scenario is unsustainable, as the environmental load surpasses the PB limit established, and therefore requires optimization and improvement (Bjørn et al., 2015; Fang et al., 2015).

Therefore, the lower the R_{ES} score, the gross difference between the actual PB-LCA value to the allocated safe operating space, greater the absolute environmental sustainability potential of the scenario under assessment. Therefore, in this sense, the scenarios with the lowest R_{ES} scores are the ones that are classified as the best production strategies under the PBs approach.

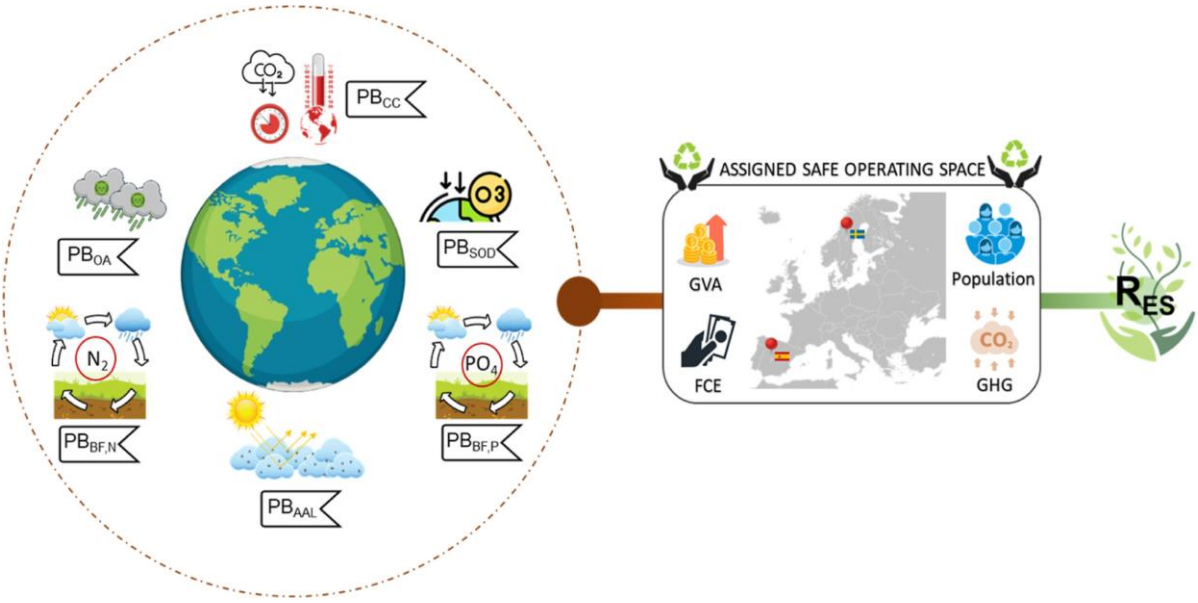

Figure 7. Methodology for performing the allocation approaches to finally obtain the ratio of sustainability (R_{ES}). Source: Own elaboration.

4.3 Assessment under a PBs approach

The PBs methodology has been applied on **Chapter 7** to assess the sustainability of the bio-based adhesives scenarios that has been developed in the **Chapter 5** and **Chapter 6**. A total number of 19 bio-adhesives scenarios has been evaluated within a PB approach, 4 about non-isocyanate polyurethanes bio-adhesives, 4 scenarios for starch bio-based adhesives, 5 for tannins and 6 alternative scenarios for soy-based bio-adhesives. Also, its

comparison with synthetic resins has been developed, considering as fossil-based adhesives urea-formaldehyde, phenol-formaldehyde and melamine-urea-formaldehyde. The rationale behind the selection of these scenarios is based on the previous research performed within the life cycle assessment methodology for the bio-adhesives production. On the other hand, the results provided by evaluating bio-based products within a planetary level are hoped to be considered as an advantaged for the identification of the contribution of industrial processes on the quality of the environment, economic profitability of the regions and level of social welfare. It could be considered as the next step to the LCA methodology, which, despite being a suitable and precise impact assessment method, it has certain limitations when it comes to establishing the global sustainability associated with a production scheme.

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SECTION III
Formaldehyde-free bio-adhesives for wood-based panels

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SUMMARY

The wood-based panel industry is one of the sectors considered strategic to meet the challenges proposed in SDGs 7, 9, 13 and 15. The integration of biotechnological approaches in forestry activities is essential to promote the use and industrialization of wood resources, processes that must take into account environmental protection and the conservation of natural heritage, thus developing alternatives that promote a sustainable use of natural resources. In this way, an ideal coexistence between forestry and industrialization would be possible. However, one of the main drawbacks identified in the production of wood-based panels, especially important gives their relevance in the furniture and decoration sector, is the need for an adhesion stage.

The adhesives used in the manufacture of these panels are a cause for concern. Restrictions imposed on the use of formaldehyde in wood panel adhesives are clearly the driving force behind the development of formaldehyde-free resins for the manufacture of wood products. Considering as a boundary condition the idea that the use of fossil-based materials should be substituted by bio-based options, there is a growing interest in the environmental evaluation of different bio-based adhesives as potential alternatives to replace petrochemical-based synthetic resins.

Section III aims to provide innovative alternatives and new trends in the field of environmentally friendly bio-adhesives for the wood panel industry. In **Chapter 5** bio-adhesives from lignocellulosic resources and pulp industries are assessed. Lignocellulosic resources encompass the use of tannins as bio-adhesive components, while in the case of pulp manufacturing facilities, the lignin used is obtained as a by-product of the kraft and Organosolv pulp manufacturing process. In **Chapter 6**, the nature of bio-based materials is now focused on the use of agri-food by-products streams, such as soy and starch.

The rationale behind the selection of these alternative bio-adhesive scenarios is justified according to the following claims: the low valorization of high value-added compounds from forestry and industrial streams (i.e. black liquor is directly used for energy valorization, thus reducing the value generation capacity of the lignin present), the huge amount of waste streams produced daily in agricultural and industrial activities (which is becoming an environmental, social and economic management problem) and the need to search for alternative raw materials to formaldehyde but with thermogravimetric properties and quality analogous to those of synthetic resins.

In this context, the objective of this section is to substantiate the suitability of alternative bio-adhesives for the production of wood-based panels. To assess their suitability, the LCA methodology has been used to environmentally analyze the production routes, with the identification of critical parameters and comparison with the scores obtained by synthetic production schemes. In addition, sensitivity analyses were also performed, aiming at suggesting improvements in the technical and environmental suitability of bio-based adhesives. Besides, a planetary boundaries evaluation has also been included in **Chapter 8**.

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Bio-adhesives derived from lignocelullosic, forestry and pulp industry by-products

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SUMMARY

The use of lignocellulosic-based feedstocks for the production of wood-based panels has experienced a growing interest, given their availability, their low procurement costs and their suitable properties to be recovered and functionalized as adhesives, as main reasons. With their use, it is possible to reduce or even avoid the use of formaldehyde, which leads to a production strategy with an expected reduction of the carbon footprint and impacts on human health.

On the other hand, at the time of the design of the production process scheme, it should be taken into account that lignin-based raw materials require a functionalization stage prior to treatment in order to activate lignin for the subsequent production stage: "cross-linking". This subsequent stage is based on the development of a covalent bond between the lignin and a specific crosslinker that allows to obtain a resin with the appropriate mechanical properties and a bonding performance analogous to that of synthetic resins.

Another renewable feedstock from the forestry sector and the cellulose industry that could be used as a source for the production of bio-adhesives are tannins, catalogued as having superior performance for the production of wood resins that are highly competitive with petrochemicals. In this case, a pretreatment is also required for its subsequent use, based on its extraction from plant resources, for which hot water pretreatment is the most widely used technique.

In this regard, **Chapter 5** is based on the evaluation of alternative lignin and tannin-based bio-adhesives scenarios by performing the conceptual design of different process alternatives and considering their potential environmental loads according to the scores obtained by the development of the LCA methodology. The different scenarios analyzed differ in the type of crosslinking agent used, as well as in the process conditions and equipment required. In addition, to be aware of the benefits that the use of these bio-based adhesive alternatives could bring, a comparison with the most commonly used synthetic resins, UF (urea formaldehyde), PF (phenol formaldehyde) and MUF (melamine urea formaldehyde), is also developed.

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5.1 Renewable alternatives to petrochemical resins: lignin and tannin

The global wood-based panel market has continuously expanded since 2014, reaching a production of 400 million cubic meters in 2018 (FAO, 2019). The synthetic resins used in the wood-based panel industry mainly belong to the formaldehyde-based types: phenol-formaldehyde (PF), urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF). Their widespread use is based on the fact that these adhesives exhibit functional properties such as flexibility, low cost, high thermal stability and resistance to water and chemicals. However, formaldehyde emissions during their production and use, associated with their fossil-based formulation, have triggered interest in sustainable and environmentally safe alternatives (Salem and Böhm, 2013; Zhang et al., 2018).

In this context, the substitution of petroleum-based chemicals with bio-based alternatives, in addition to the reduction of formaldehyde emissions, have been identified as major targets in the sustainability strategy of the adhesives and wood-based panel industries in the short to medium term. Legislation is becoming increasingly strict in terms of its allowable emission limits, given the harmful effects formaldehyde can cause on human health as well as the environment. The main reason on the development of eco-friendly wood adhesives are based on environmental sustainability, costs savings, recyclability, reusability and health benefits, in comparison with synthetic resins.

Therefore, the development of formaldehyde-free bio-adhesives derived from waste streams and unusable resources is considered an innovative option with a strong market presence. However, the formulation of bio-adhesives for the wood-based panel industry is at an early stage of development, mainly at the laboratory scale (Chen et al., 2020b; Gouveia et al., 2020; Pizzi, 2016a). To this end, scaling up to a higher production capacity is required to evaluate and compare the potential of bio-adhesives in the wood-based panel market. Consequently, process modelling in the SuperPro Designer® tool has been considered to develop the conceptual design of the manufacturing processes.

Throughout this chapter, the evaluation of alternatives based on the use of by-products or residues from the wood and forestry sector are developed, considering both lignin and tannins. It should be considered that the use of these raw materials in the formulation of bio-adhesives requires carrying out a series of steps for their functionalization, to achieve the mechanical properties required. This functionalization process enables to the formation of high hardness urethane bonds, which give rise to non-isocyanate polyurethane resins (NIPU), which have mechanical properties suitable for their application in the panel bonding stage (Saražin et al., 2020).

Despite the numerous papers reporting different formulation protocols for bio-adhesives production (Amari et al., 2021; Li et al., 2016; Moubarik et al., 2010a; P. Navarrete et al., 2010; Ndiwe et al., 2019; Ramires and Frollini, 2012), there is a need for environmental information on the impacts associated, especially important at an early stage of development. We cannot ignore the fact that if the production process has a greater environmental impact than its petrochemical counterparts, there are few options for new bio-adhesives to be considered feasible, viable and environmentally sustainable alternatives (Arias et al., 2020; Arias et al., 2021). Different research reports have demonstrated the benefits of considering bio-based adhesives instead of synthetic resins, being biodegradability, lower carbon footprint, reduced toxicity and positive impact to climate change the main advantages that stand out (Heinrich, 2019).

To this end, once the bio-adhesive production processes have been designed and the input and output flows estimated, the Life Cycle Assessment methodology has been considered to provide extensive information on the environmental indicators in the

different impact categories based on a detailed analysis of the inventory of raw materials, products, energy and emissions associated with a product or process. By developing this assessment, it may be possible to identify which of the evaluated bio-adhesive alternatives has the best environmental performance, i.e., the one with the lowest environmental impact.

5.2 Description of the scenarios under evaluation

Moving forward in the description of the scenarios, considering a definition of the process schemes and stages required for the formulation and production of bio-adhesives, two main sections are included, one referring to lignin-based resins and the other based on tannin-based bio-adhesive alternatives.

5.2.1 Lignin bio-adhesives

In the case of lignin bio-adhesives, the source of this lignin comes from two main waste streams: black liquor from the Kraft pulp manufacturing process, so Kraft lignin is obtained, and Organosolv lignin from the Organosolv process.

Kraft lignin is one of the most common waste streams obtained in pulp processing, accounting for 85% of the total lignin from industrial processes, approximately (Chen, 2015). It is characterized by being insoluble in water and in most solvents, with the exception of very alkaline ones (Hemmilä et al., 2017). Regarding its main properties, it has a molecular weight around 3500 g/mol, a transition temperature in the range of 90 to 180°C and a high content of aliphatic hydroxyl groups compared to other types of lignins (El Mansouri and Salvadó, 2007; Kun and Pukánszky, 2017; Solt et al., 2019a).

In the case of Organosolv lignin, it is a water-insoluble lignin obtained through the Organosolv pulp manufacturing process based on aqueous organic solvents to carry out the pulping process (Liu et al., 2022). Its main advantage is the absence of sulfur in the process, which implies a reduction of environmental loads, since organosulfur compounds are avoided (Shrotri et al., 2017). Regarding its main characteristics, it has a molecular weight between 700-1500 g/mol, low dispersity, medium to high transition temperatures, between 70 to 170ºC, and a significant amount of phenol hydroxyl functional groups (Sathendra et al., 2022).

However, for the lignins to be applicable in the production of bio-based adhesives, their functionalization is necessary. In this sense, two main activation processes have been considered: (1) glyoxalation and (2) carbonation. For both processes, lignin must first be precipitated from the black liquor of the pulping process under acidic conditions, washed and dried, to obtain a lignin powder.

5.2.1.1 Glyoxalated KL and OSL bio-adhesives

In the case of process (1), the lignin powder was glyoxalized with solutions of water, NaOH (30%) and glyoxal (40%), requiring continuous agitation for 8 h at 58ºC (Navarrete et al., 2010). Afterwards the functionalization stage, the crosslinking process is required to formulate the final bio-adhesive. In the case of kraft lignin, the glyoxalate lignin is mixed with polyethylenimine (PEI) for 40 min at room temperature, and considering a weight ratio of 5:1 lignin:PEI (Geng and Li, 2006), while when using the glyoxalated Organosolv lignin, furfural is used as crosslinker under acidic conditions at 90ºC for 1 h (Kautto et al., 2013). It is worth mentioning that, for this last scenario, furfural has been considered to be produced through a bio-based scheme, therefore derived from lignocellulosic biomass and following a biorefinery approach (Bello et al., 2018).

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5.2.1.2 Carbonated KL and OSL bio-adhesives

In developing the activation alternative (2), dimethyl carbonate (DMC), which is the simplest non-cyclic aliphatic carbonate, is used to develop a nucleophilic acyl scission substitution reaction (Saražin et al., 2021; Xi et al., 2018). As a non-isocyanate is used for the formulation of these bio-adhesives, they could be named as Non-Isocyanate Polyurethane (NIPU) bio-adhesives. It should be mentioned that various reaction mechanisms could be developed using DMC, but in this case, the mechanism is based on the reaction with the phenolic groups available on the molecular structure of the lignin, leading to the release of methanol in the reaction scheme. This second activation route is considered an effective method since it leads to an improvement of the thermal stability, mechanical properties and increased affinity of the bio-adhesive polymer blend (Duval and Avérous, 2020; Feng et al., 2021; Sen et al., 2015; Xiong et al., 2020). While activated, both lignins will undergo the same crosslinking step, based on the addition of a diamine compound, namely hexamethylenediamine (HDMA). The reaction scheme is based on a first reaction with the phenolic groups of the lignin, followed by the reaction of the amino group with the intermediate, forming urethane bonds and releasing methanol from the methoxy group of the intermediate and the hydrogen atom of the HDMA molecule (Khiari et al., 2016; Pizzi, 2016b; Sen et al., 2015). **Figure 1** represents a simple mechanism for the formulation of the lignin-based NIPU bio-adhesives.

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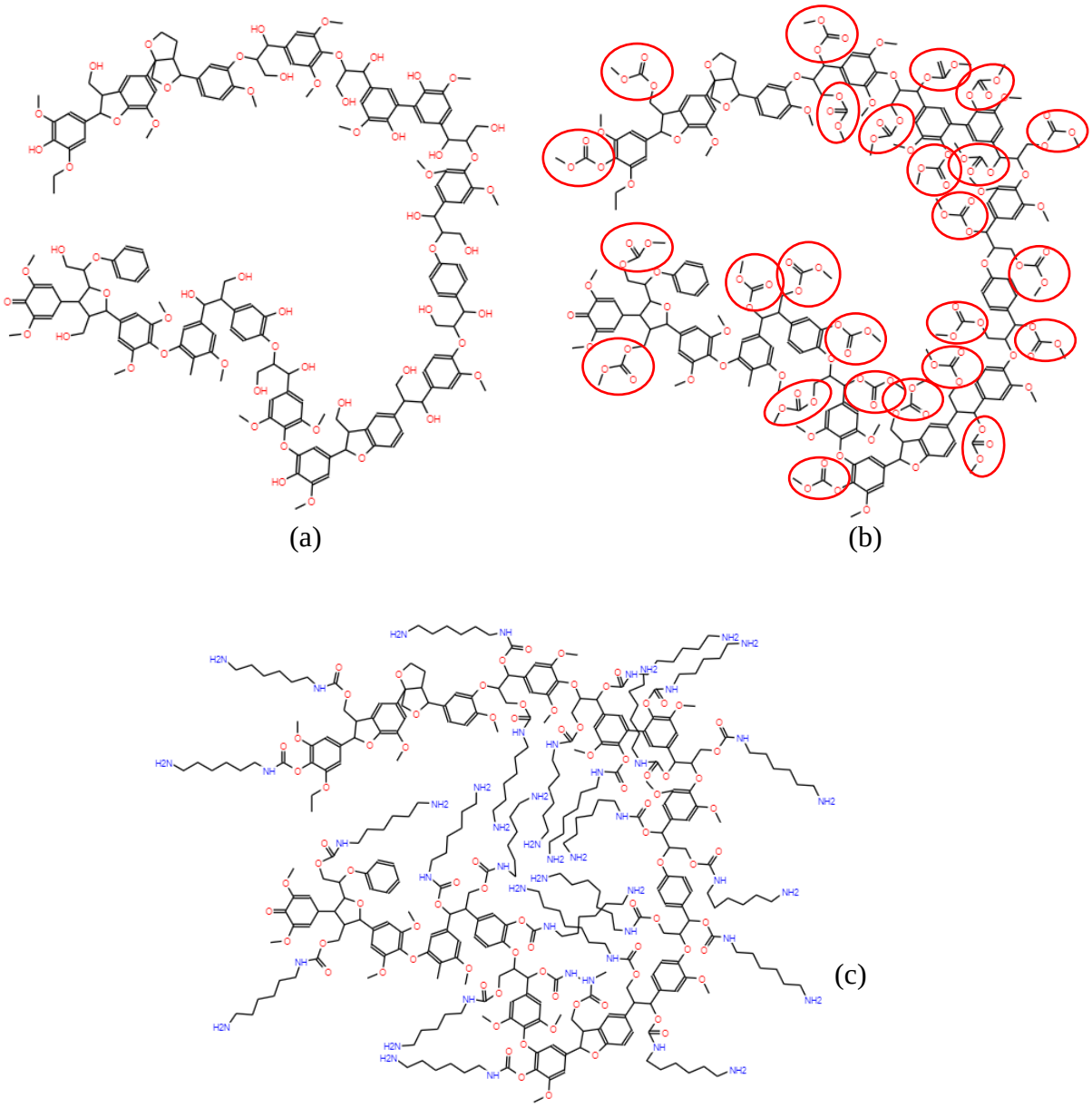

Figure 1. Representation of a simple mechanism for the formulation of the OSL-NIPU bio-adhesives. Source: Own elaboration.

5.2.2 Tannin bio-adhesives

The tannin-based alternative has experienced significant interest (Thébault et al., 2014) not only because of its renewable origin and the wide variability of manufacturing process conditions (Pizzi, 2006), but also given its superior performance of the final product, which is highly competitive with petrochemical resins. Two alternatives can be identified: condensed tannins (Pizzi, 1982), whose structure is based on polymers of flavanol units (Schofield et al., 2001) and hydrolysable tannins (Spina et al., 2013), which are esters of carboxylic acids and sugars. Although both could be used as substitutes for phenol-formaldehyde resins, hydrolysable tannins represent a worse option, since they have a low level of phenolic substitution and lack polymeric structure (Pizzi, 1982). As in the case of lignin, tannins also need to be extracted from different parts of the plant

(Hemmilä et al., 2017) and hot water extraction is the most widely used method among the different options available (Bianchi et al., 2015; Ding et al., 2017; González-García et al., 2016; Kilpelainen et al., 2019; Krogell et al., 2012).

To this end, five scenarios of tannin bio-adhesive processes have been considered, according to the use of different chemicals for the formulation of resins: paraformaldehyde, glyoxal, hexamine, ammonium hydroxide and hexamethylenediamine (HDMA). These chemicals are used as crosslinking agents and hardeners, which can promote the formation of covalent and ionic bonds between polymers, thus creating high molecular weight polymer chains (Solt et al., 2019a). This process of conversion from a short polymer chain to a dimensional network is called adhesive curing.

In all scenarios of the proposed bio-adhesives, the first stage of the production process consists of the extraction of the tannin from the bark using the hot water extraction method as the most recurrently used method. Although the addition of chemicals is not necessary, the process involves high energy consumption. The information on the manufacturing process for obtaining condensed tannin has been taken from González-García et al. (2016). This process includes not only the extraction of the condensed tannin, but also the background activities associated with forestry activities and the management of waste streams. Although the addition of chemicals is not necessary, the process involves a high consumption of energy (Ding et al., 2017).

Mass and energy flows of the different tannin bio-adhesive processes are estimated on the basis of laboratory-scale data and implemented through Aspen Hysys® as a process simulation software. The modelling of the reaction unit is the main stage of a facility producing 24 t/d, which is in the range of the production capacity of formaldehyde-based adhesives in other studies: 15,000 t/year (Yang and Rosentrater, 2019a, 2021).

5.2.2.1 Tannin-paraformaldehyde (TP) bio-adhesive

The manufacturing process of the bio-adhesive is formulated from the following mixture: extracted tannin, water, paraformaldehyde and NaOH (Ballerini et al., 2005). In substitution of formaldehyde, paraformaldehyde is considered in this alternative as it could be rapidly depolymerized under alkaline conditions (Zhou and Du, 2020). One of the advantages of this bio-adhesive is based on the fact that no pre-reaction steps are needed, they are simply mixed in a glue mixer just before the mixture is used as an adhesive. The hardening reaction occurs exclusively during the hot-pressing phase of the wood panels.

5.2.2.2 Tannin-glyoxal (TG) bio-adhesive

Tannin-glyoxal bio-adhesives have potential for the formulation of adhesive polymers used for wood bonding (Khiari et al., 2017), where glyoxal is a substitute of formaldehyde as a hardening agent. The glyoxylation reaction consists of the formation of cross-linked bridges between glyoxal and the aromatic sites of the tannin molecular structure. The inventory data of tannin-glyoxal bio-adhesive includes extracted tannin, water, glyoxal and NaOH as main inputs. As with the tannin-paraformaldehyde adhesive, the hardening reaction occurs exclusively during the hot-pressing stage of the wood-based panels, so no pre-reaction stage is required.

5.2.2.3 Tannin-hexamine (TH) bio-adhesive

Hexamine can be also an alternative hardener that does not lead to formaldehyde emissions (Pena et al., 2009). The cross-linking reaction process between hexamine and tannins takes place through the formation of reactive or intermediate fragments of hexamine and their reaction with the phenolic nuclei of polyflavonoid tannins

(Mosiewicki et al., 2004). In this scenario the bio-adhesive is formulated based on extracted tannin mixed with water, hexamine and NaOH.

5.2.2.4 Tannin-NIPU based bio-adhesive.

Polyurethanes are classified as thermosetting polymers, which are composed of organic units linked by urethane (or carbamate) bonds. They are versatile polymers of strong chemical structure (Lanaro et al., 2018), with an outstanding role as binders in medium-density fiberboards, laminated wood, particleboards, among others (Madhav et al., 2019). Although its use is widespread, currently the formulation of polyurethanes that do not contain isocyanates in its structure is pursued, due to the need to eradicate phosgene in its production process (Figovsky et al., 2013; Kathalewar et al., 2013). Thus, the production of so-called non-isocyanate polyurethanes (NIPU) is based on the chemical reaction between carbonates and primary amino groups, forming a cross-linked polymer with a lower environmental impact compared to conventional polyurethanes (Figovsky et al., 2013). In addition, other positive characteristics of NIPU polymers are structural and thermal stability, water tolerance and chemical resistance. Based on these assumptions, two tannin-based scenarios based on NIPU polymers have been proposed.

5.2.2.4.1 Tannin-NIPU with ammonium hydroxide (TNA) bio-adhesive

There are different methods for preparing NIPU polymers, but one of the most widespread is the polycondensation reaction of cyclic carbonates and primary amines, which results in the production of a polymer chain with hydrogen bonds (Datta and Włoch, 2016). The formulation of the bio-adhesive starts with the condensation of the tannins in an ammonium hydroxide medium (Thébault et al., 2017), becoming a viscous mixture with the formation of nitrogen bonds between the flavonoid molecules of the tannins. The tannin extract is then mixed with dimethylcarbonate (DMC), which requires a reaction time of 2 h under mechanical agitation and 90°C. At this stage, the carboxymethylation process of the hydroxyl phenolic groups of DMC takes place. This mixture is added to the condensed amino tannins for the final formulation of the bio-adhesive.

5.2.2.4.2 Tannin-NIPU with HDMA (TNH) bio-adhesive

The formulation of this type of tannin-NIPU bio-adhesive is similar to the previous one, with the difference that HDMA is used for the formation of the urethane bonds. In this case, tannins are mixed with deionized water and DMC and the mixture is heated to 65°C for 60 min (Chen et al., 2020c). Finally, for the formation of the urethane bonds, HDMA is added to the mixture at 90°C for 2 h. The last step is to reduce the temperature of the adhesive to room temperature (Chen et al., 2020c). For the case of HDMA, the modelling of its production process was also performed from the available data reported in the literature (Dros et al., 2015). The main reasons for selecting the bio-based adhesives with tannins mentioned and discussed are included in **Table 1.**

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Table 1. Justification of the selection of the aforementioned tannin bio-adhesives.

Tannin bio-adhesive alternative	Justification
Tannin-paraformaldehyde (TP)	Simplicity in the formulation of the bio-adhesive. No pre-reaction steps required
Tannin-glyoxal (TG)	Glyoxal is an adequate hardening agent to be used as substituted to formaldehyde, being less toxic. No pre-reaction steps required
Tannin-hexamine (TH)	No formaldehyde emission Strong intermolecular forces formed in the cross-linking reaction.
Tannin- NIPU with ammonium hydroxide (TNA)	The use of non-isocyanate polyurethanes leads to the formation of strong polymers with lower environmental impacts. Improvement on mechanical properties: better thermal stability, water tolerance and chemical resistance.
Tannin-NIPU with HDMA (TNH)	Better mechanical properties. Formation of strong urethane bonds.

5.3 Description of system boundaries and process inventories for LCA

In accordance with the system boundaries, a "cradle-to-gate" approach has been considered for the collection of inventory data (**Figure 2** corresponds to lignin bio-adhesives alternatives and **Figure 3** for the tannin ones), i.e., stages from the extraction of materials and resources to the factory gate were considered. This approach is in line with the requirements of environmental product declarations (Cao, 2017). Production and maintenance of infrastructure and transportation activities were left out of the system boundaries, as their contribution to the overall process environmental loads are not significant (Arias et al., 2020; Yang and Rosentrater, 2021).

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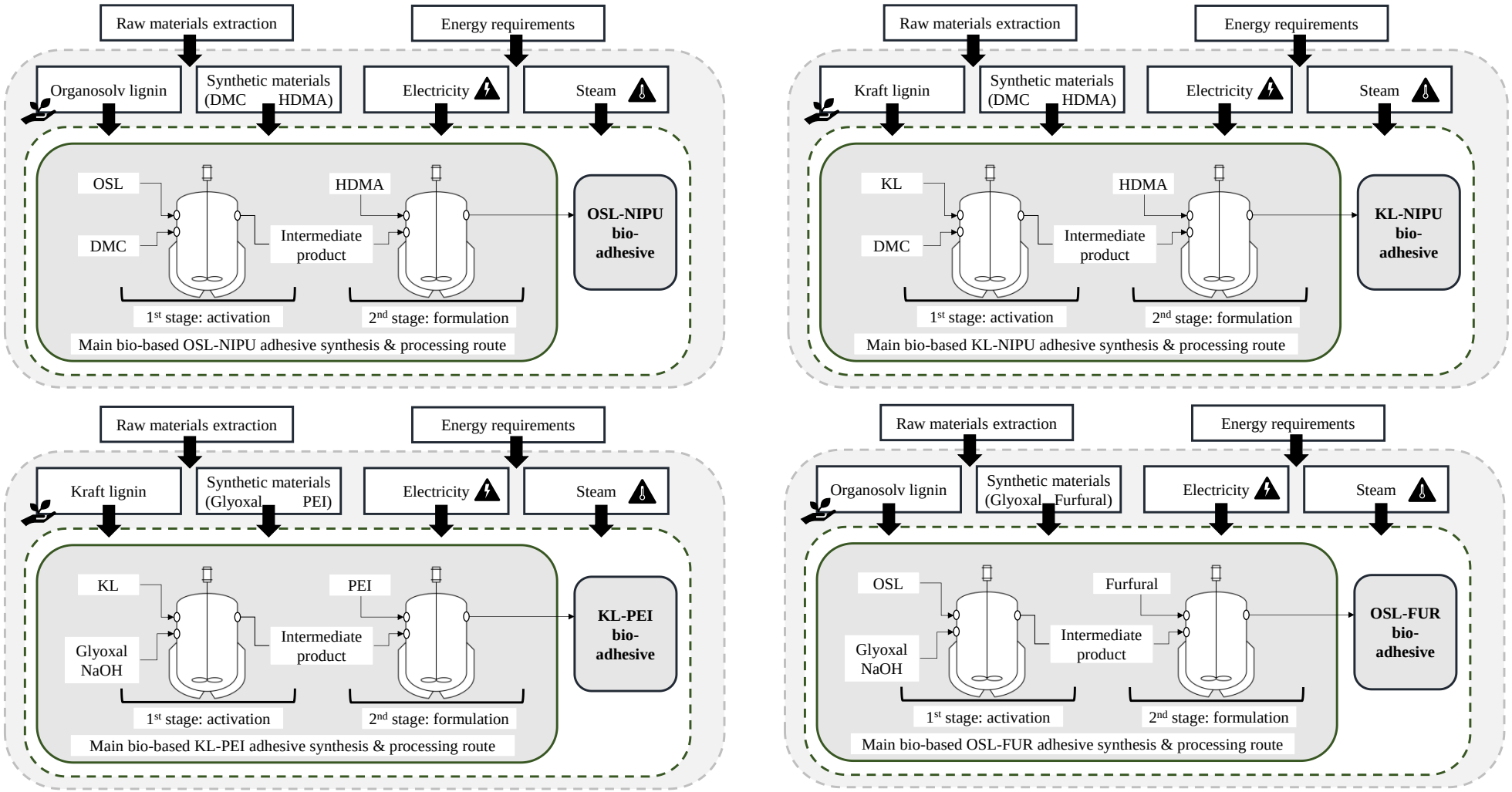

Figure 2. System boundaries considered for the lignin-based bio-adhesives.

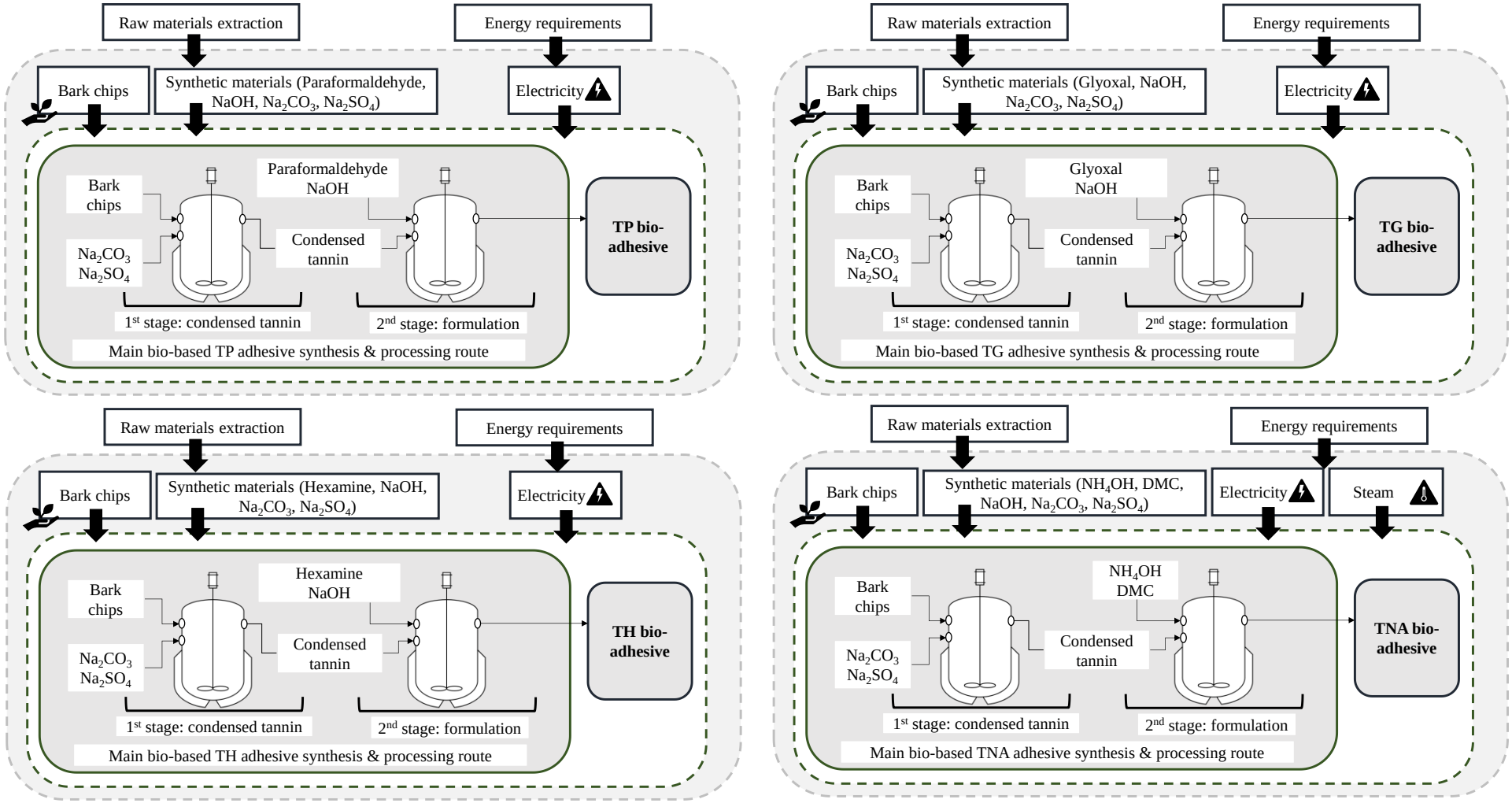

Figure 3. System boundaries considered for the tannin-based bio-adhesives.

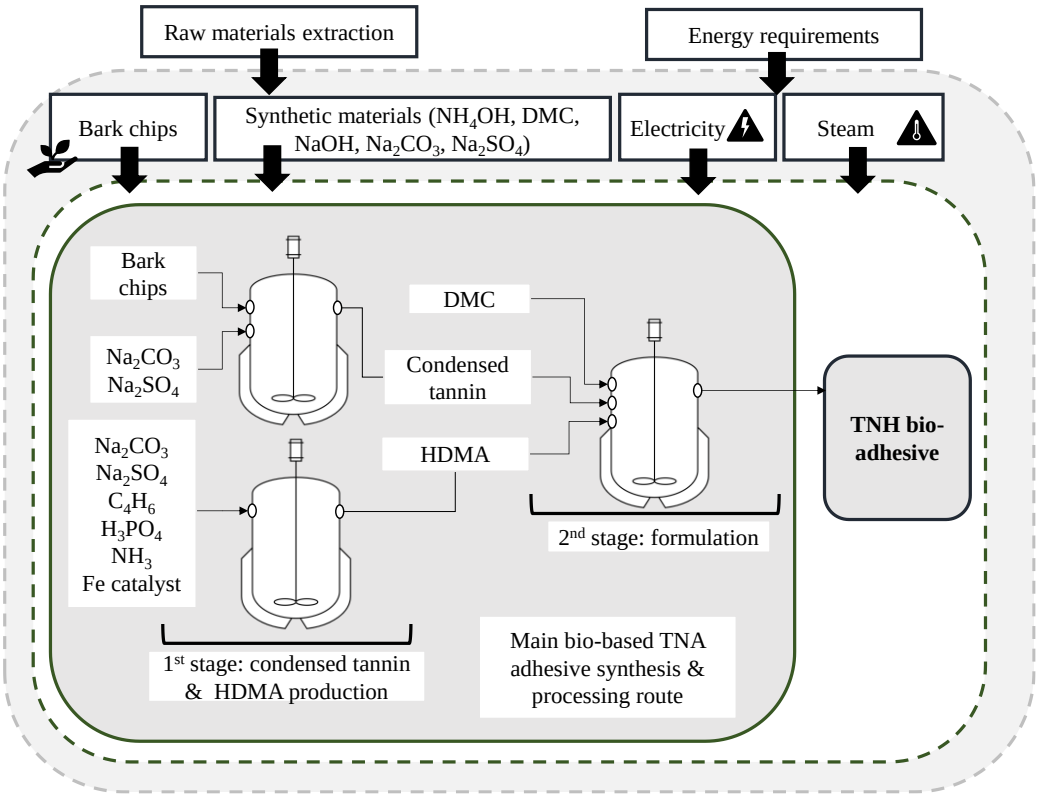

Figure 4. System boundaries considered for the tannin-based bio-adhesives (continuation).

In order to exemplify the mechanism, **Figure 5** represents a simple mechanism for the formulation of the tannin-based NIPU bio-adhesives, considering the last scenario under assessment, the one using HDMA as crosslinker.

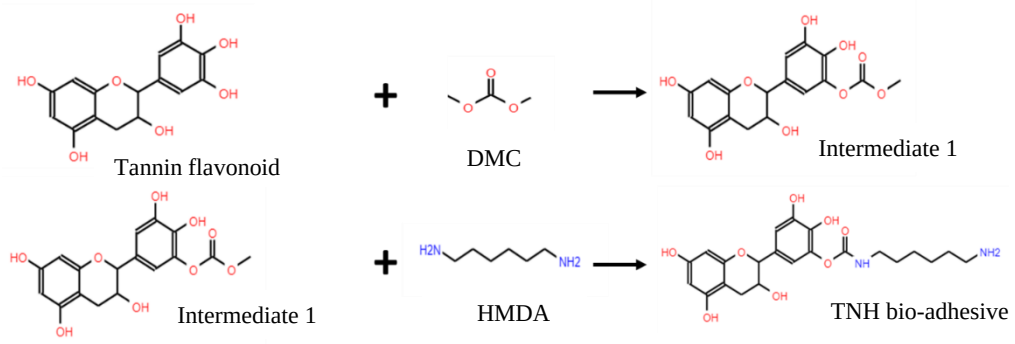

Figure 5. Representation of a simple mechanism for the formulation of the TNA bio-adhesives.

5.3.1 Definition of the process inventories for LCA

Once the system boundaries are defined, life cycle inventories are calculated, considering all inputs and outputs corresponding to the foreground systems of both lignin and tannin bio-based adhesives, considering the production of 1 kg of bio-adhesive as the

functional unit. The life cycle inventories for each of the alternatives are depicted in **Table 2** to **Table 10.**

Table 2. Main inputs and outputs values considered for performing the life cycle inventory for OSL-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
OSL	0.18	kg	OSL-NIPU bio-adhesive	1	kg
DMC	0.12	kg			
HDMA	0.25	kg			
Water	0.68	kg			
Electricity/heat			*Emissions to air*		
Steam	0.41	kg	Water, vapor	0.13	kg
Electricity	0.54	kWh	Methanol	0.11	kg

Table 3. Main inputs and outputs values considered for performing the life cycle inventory for KL-NIPU adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
KL	0.19	kg	KL-NIPU bio-adhesive	1	kg
DMC	0.13	kg			
HDMA	0.26	kg			
Water	0.60	kg			
Electricity/heat			*Emissions to air*		
Steam	1.06	kg	Water, vapor	0.03	kg
Electricity	3.81	kWh	Methanol	0.12	kg

Table 4. Main inputs and outputs values considered for performing the life cycle inventory for KL-PEI adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
KL	0.28	kg	Glyoxalated lignin	0.74	kg
NaOH	0.04	kg			
Glyoxal	0.03	kg	*Waste to treatment*		
Water	0.47	kg	Wastewater	0.05	L
Electricity/heat			Incineration	0.03	kg
Steam	102.9	kJ	*Emissions to air*		
Electricity	12.52	kWh	Glyoxal	3.40	g
INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Glyoxalated lignin	0.74	kg	KL-PEI bio-adhesive	1	kg
PEI	0.37	kg			
Electricity/heat					
Steam	102.9	kJ	*Waste to treatment*		
Electricity	0.74	kWh	Solid waste to incineration	0.11	kg

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Table 5. Main inputs and outputs values considered for performing the life cycle inventory for OSL-Furfural adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
OSL	0.40	kg	Glyoxalated lignin	1.06	kg
NaOH	0.06	kg			
Glyoxal	0.05	kg	*Waste to treatment*		
Water	0.67	kg	Wastewater	0.05	L
Electricity/heat			Incineration	0.04	kg
Steam	146.6	kJ	*Emissions to air*		
Electricity	30.4	kWh	Glyoxal	4.80	g
INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Glyoxalated lignin	1.06	kg	OSL-FUR bio-adhesive	1	kg
PEI	0.06	kg			
Electricity/heat					
Steam	10.47	kJ	*Waste to treatment*		
Electricity	2.31	kWh	Solid waste to incineration	0.11	kg

Table 6. Main inputs and outputs values considered for performing the life cycle inventory for TP bio-adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Condensed tannin	0.40	kg	TP bio-adhesive	1	kg
Paraformaldehyde	0.05	kg			
NaOH	0.05	kg			
Water	0.50	kg			
Electricity/heat					
Electricity	17.75	MJ			

Table 7. Main inputs and outputs values considered for performing the life cycle inventory for TG bio-adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Condensed tannin	0.39	kg	TH bio-adhesive	1	kg
Glyoxal	0.10	kg			
NaOH	0.04	kg			
Water	0.47	kg			
Electricity/heat					
Electricity	17.75	MJ			

Table 8. Main inputs and outputs values considered for performing the life cycle inventory for TH bio-adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Condensed tannin	0.40	kg	TH bio-adhesive	1	kg
Hexamine	0.06	kg			
NaOH	0.04	kg			
Water	0.49	kg			
Electricity/heat					
Electricity	17.75	MJ			

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Table 9. Main inputs and outputs values considered for performing the life cycle inventory for TNA bio-adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Condensed tannin	0.24	kg	TNA bio-adhesive	1	kg
$NH_4)OH$	0.07	kg			
DMC	0.68	kg			
Water	0.19	kg			
Electricity/heat					
Heat	38	kJ	*Emissions to air*		
Electricity	0.12	kWh	Methanol	0.18	kg

Table 10. Main inputs and outputs values considered for performing the life cycle inventory for TNH bio-adhesive.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Butadiene	0.55	kg	HDMA	1	kg
Phosphoric acid	5.00	g			
Ammonia	0.41	kg			
Dihydrogen	0.07	kg			
Sodium bisulfite	0.11	kg			
Sodium sulfite	0.07	kg	*By-products*		
Catalyst, Fe	6.00	g	Heavy amines	13.07	g
Electricity/heat			Imines (hexamethylenimine)	4.06	g
Cooling water	0.67	m^3			
Steam	8.99	kg	*Emissions to air*		
Electricity	9.32	kWh	CO_2	0.62	kg
INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Condensed tannin	0.23	kg	TNH bio-adhesive	1	kg
Deionized water	0.19	kg			
DMC	0.21	kg			
HDMA	0.31	kg			
Water	0.13	kg			
Electricity/heat					
Heat	547	kJ	*Emissions to air*		
Electricity	0.29	kWh	Methanol	0.05	kg

5.3.2 Some assumptions and considerations

The Ecoinvent® database was used as the main source of background data. Since not all components required for the formulation of bio-adhesives are available in the database, certain substitutes had to be considered. Ethylenediamine was considered an analogous product to DMC, since their production process is similar to a large extent and, therefore, it is foreseeable that their environmental burdens would be analogous. And, in the case of DMC and other bio-based, water and energy resources, inventory data are available for the development of their environmental assessment. As for electricity, medium voltage has been considered, as it is sufficient for the energy requirements necessary for the bio-adhesive formulation process.

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5.4 Environmental assessment of the alternatives

In order to evaluate the best procedure for the formulation the bio-based adhesives, it is necessary to perform a comparative environmental analysis. ReCiPe Midpoint has been the selected methodology to determine the environmental impact values for each of the proposed alternatives (**Table 11**). But, at the same time, it is important to develop a more exhaustive study for each of the proposed processes to analyze the contribution of each input and output included within the system boundaries of each alternative under evaluation. These analyses are included in the following sections. On the other hand, a comparative evaluation using the ReCiPe EndPoint methodology has also been assessed for the bio-adhesive alternatives.

Table 11. Characterization results of the lignin and tannin bio-based adhesives alternatives considering ReCipe Midpoint as the calculation methodology.

Impact category	Unit	OSL-NIPU	KL-NIPU	KL-PEI	OSL-FUR	TP	TG	TH	TNA	TNH
GW	kg CO_2 eq	1.98	3.63	8.34	15.54	2.95	3.10	3.15	3.52	3.69
SOD	mg CFC_{11} eq	0.92	1.66	4.33	8.49	16	16	17	19	3.98
TA	g SO_2 eq	5.48	11.19	38.17	77.16	152	156	159	163	53
FE	g P eq	0.61	1.99	6.89	15.26	27	28	28	27	1.38
ME	g N eq	0.93	1.06	1.79	1.08	2.16	2.19	4.24	2.07	0.11
TET	kg 1.4-DCB	3.13	4.09	13.20	16.52	2.01	2.04	2.39	2.75	4.67
FET	kg 1.4-DCB	0.02	0.06	0.28	0.56	0.72	0.73	0.73	0.77	0.04
MET	kg 1.4-DCB	0.03	0.08	0.38	0.76	0.10	0.10	0.10	0.11	0.06
HCT	kg 1.4-DCB	0.05	0.12	0.43	0.88	0.14	0.15	0.15	0.14	0.08
HNCT	kg 1.4-DCB	0.86	2.54	6.71	12.89	2.50	2.51	2.53	2.53	1.44
FRS	kg oil eq	0.80	1.26	2.49	3.94	0.80	0.88	0.89	1.45	1.25

5.4.1 Environmental profile of the OSL-NIPU bio-adhesive

Two main hotspots associated with the bio-adhesive production procedure can be identified (**Figure 6**): the use of hexamethylenediamine (HMDA), required as the crosslinker for the adhesive formulation, to favour the urethane bonds, together with the energy required for agitation and maintenance of the temperature (50ºC for the carbonation process, and 90ºC for the bonding between the amino group of HMDA and the carbonated intermediate product). In addition, energy is also required to increase the solids content of the bio-adhesive up to 46%. In this case, the environmental contribution of HMDA is significantly higher and stands out compared to the other components of the life cycle inventory. The reason for this higher contribution is based on the fact that the OSL is directly used for the formulation of the bio-adhesive, i.e., it does not require a pre-treatment stage for its use as a resource for the formulation of the adhesive. This lack of pretreatment greatly favors this scenario, as a lower expected environmental impact could be achieved, not only by avoiding the consumption of non-renewable resources, i.e. the

chemicals needed for extraction and energy requirements, but also the associated emissions. Therefore, although the amount of HDMA used in the formulation of the bioadhesive is equivalent, its impact is not, since the fact that the OSL has a lower contribution entails a more notable environmental contribution from the other components.

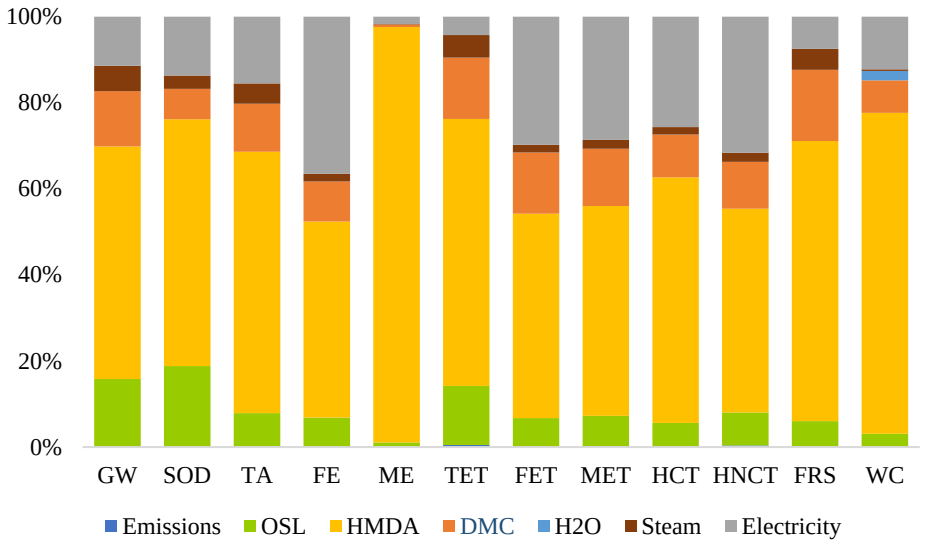

Figure 6. Environmental profile and individual contributions of the OSL-NIPU adhesive considering the Recipe Midpoint methodology.

5.4.2 Environmental profile of the KL-NIPU bio-adhesive

Although the operating conditions are analogous to those of the OSL-NIPU bioadhesive, the contribution of energy requirements to the environmental profile of the KL-NIPU bioadhesive is higher than the previous option presented above. This increase in the electricity consumption of the process could already be observed in the inventories of both alternatives, where in the case of OSL a total of 0.54 kWh/kg bioadhesive is required, this value is almost eight times higher for the KL-based adhesive, amounting to 3.81 kWh/kg bioadhesive. The reason behind this increase is based on the different molecular weights of the lignins. While in the case of OSL, its average molecular weight is around 4689 g/mol, in the case of KL its value rises to 7916 g/mol. A higher molecular weight implies a greater difficulty in maintaining the homogeneity of the crosslinking reaction medium between the components contributing to the bioadhesive formulation. Therefore, the greater the molecular mass, most difficulty on the homogenization and higher requirements of stirring power which, consequently, will need a higher energy demand, leading to a greater contribution to the environmental profile (**Figure 7**). Finally, it is worth mentioning that the contribution of HDMA to the bioadhesive profile remains high.

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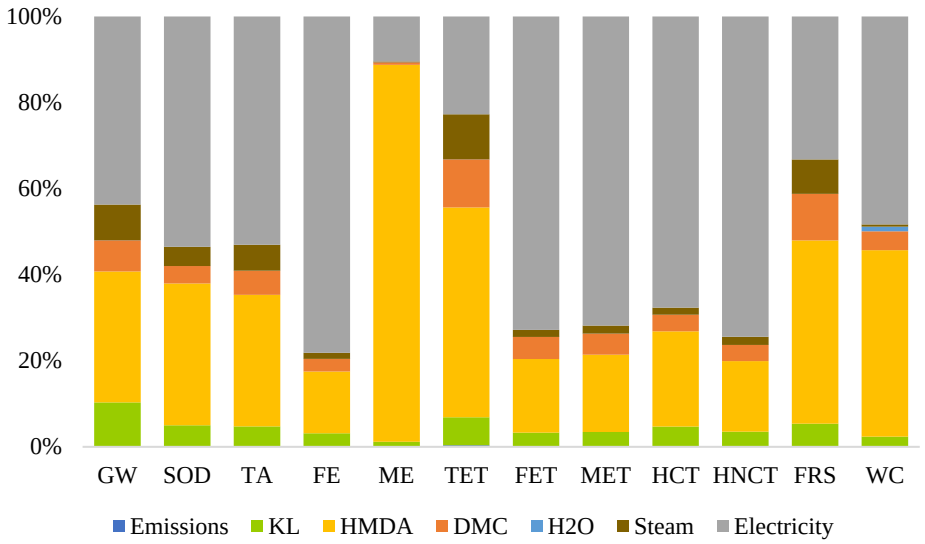

Figure 7. Environmental profile and individual contributions of the KL-NIPU adhesive considering the Recipe Midpoint methodology.

5.4.3 Environmental profile of the KL-PEI bio-adhesive

The environmental profile of the bio-based adhesive formulated using KL and PEI as crosslinking agent is depicted in **Figure 8**. As can be seen, glyoxylated lignin is the largest contributor to environmental burdens in most of the impact categories evaluated, with a percentage contribution ranging from 54% to 86% (with the exception of the ME impact category, where the percentage contribution is reduced to 24%).

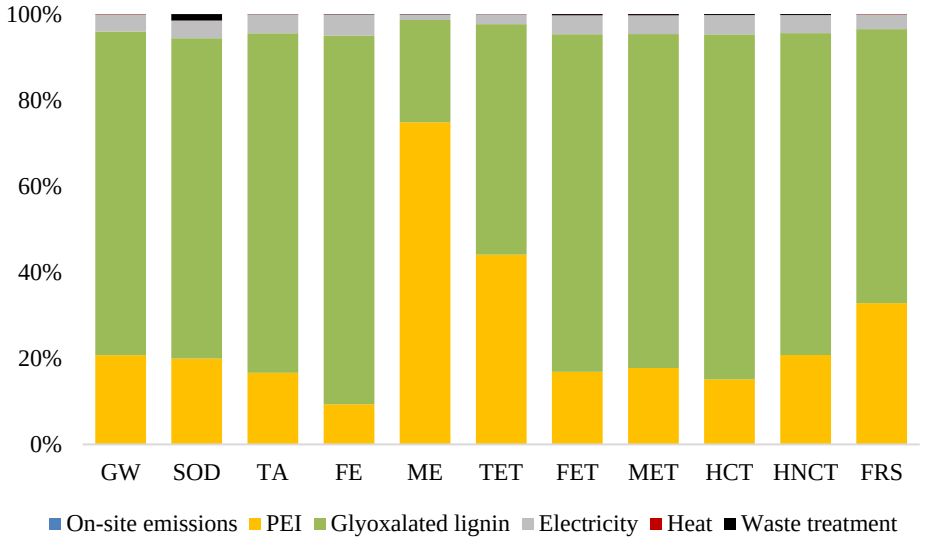

Figure 8. Environmental profile and individual contributions of the KL-PEI adhesive considering the Recipe Midpoint methodology.

The reason for this huge impact derives from the significant energy requirements for the glyoxalation of kraft lignin, as can be seen in **Figure 9**, which includes the environmental profile of the KL pretreatment step for activation using glyoxal. The huge amount of electricity used derives mainly from the agitation needed for 8 h, which is the process time required for the activation and functionalization of lignin. On the other hand,

the contributions associated with energy/heat requirements and waste treatment are almost negligible (**Figure 8**) but, for the case of on-site emissions to the atmosphere, attention should be paid to the TET impact category, for which glyoxal emissions account for a contribution amounting to 18% of the total impact load.

On the other hand, for the bio-adhesive profile, also certain contribution is observed by the use of PEI as crosslinking agent in the impact categories of ME (about 75% of contribution), TET (44%) and FRS (33%), particularly due to emissions of ammonium and nitrate and the energy demands for their production. Its production scheme is based on the subsequent manufacture of aziridine, an organic chemical derived from petroleum (Williams and Hillmyer, 2008).

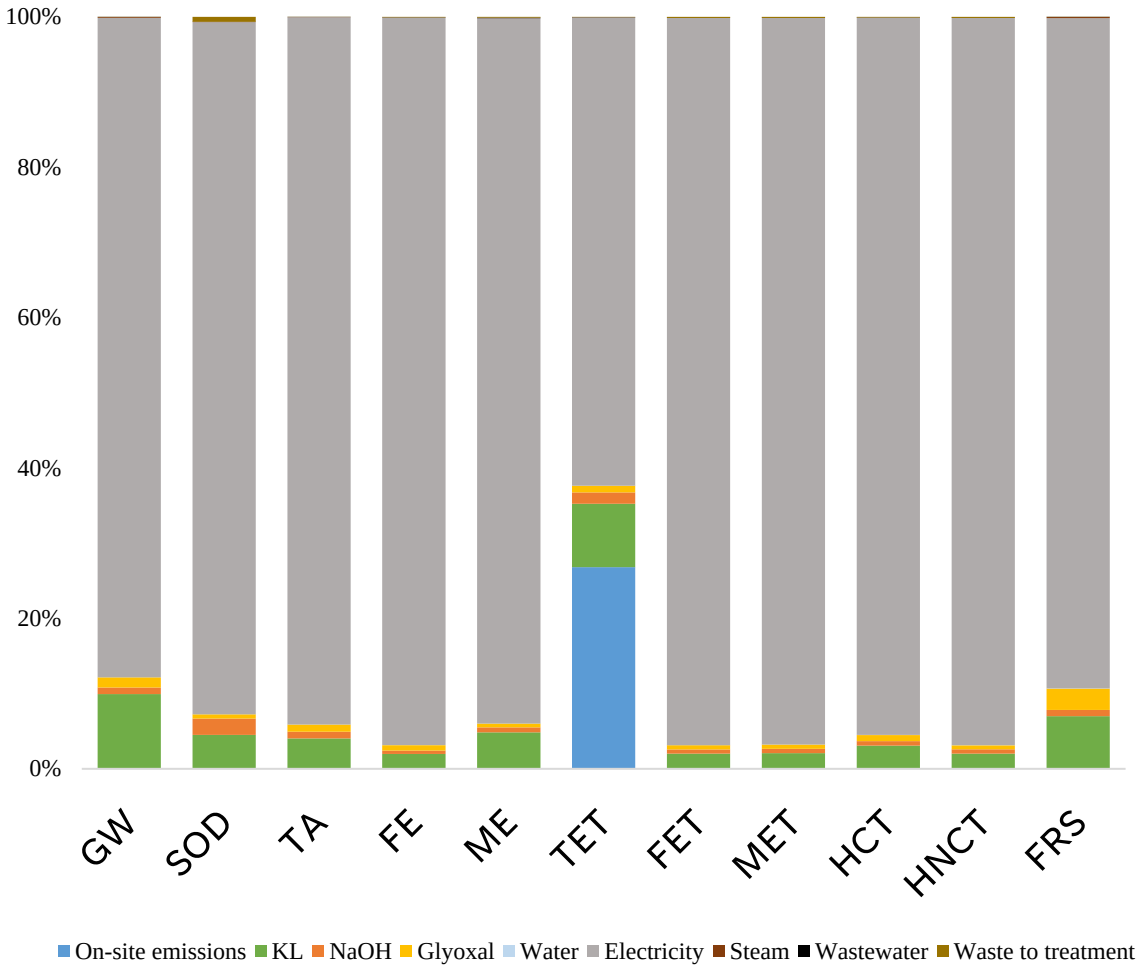

Figure 9. Environmental profile and individual contributions of the glyoxalation of kraft lignin considering the Recipe Midpoint methodology.

5.4.4 Environmental profile of the OSL-FUR bio-adhesive

Figure 10 includes the distribution of the impacts loads by impact category for the OSL-FUR bio-adhesive. As can be seen, and similar to what occurred in the previous scenario evaluated (KL-PEI bio-adhesive), the pretreatment stage for the

functionalizadion of the organosolv lignin to obtain glyoxalated lignin, is the one that implies the highest contribution. The reasons behind this impact are just the same as those mentioned for **Figure 9**: electricity requirements. On the other hand, as regards the contribution of the waste stream, the organosolv lignin does not have a significant contribution to the profile obtained, with percentages ranging between 1% and 6%. In the case of furfural, its production by biological means implies an insignificant contribution.

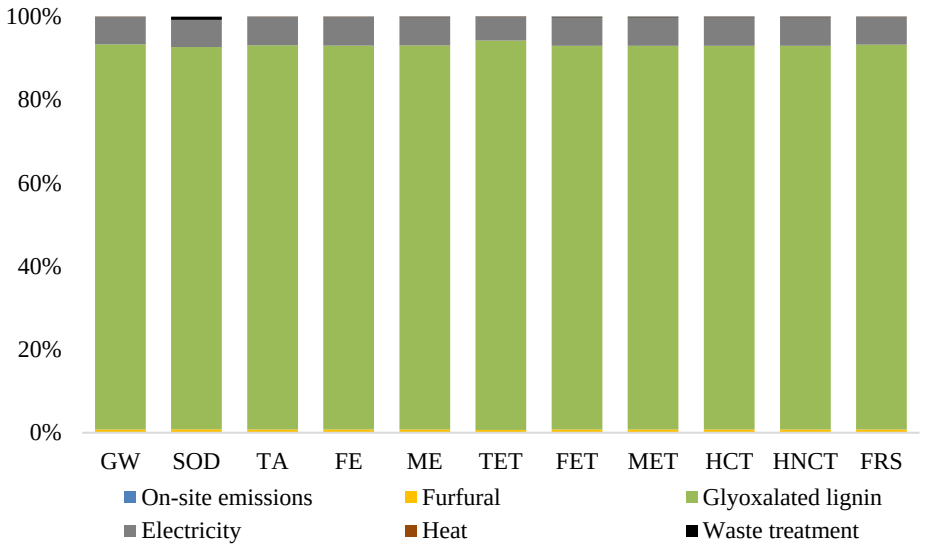

Figure 10. Environmental profile and individual contributions of the OSL-FUR bio-adhesive considering the Recipe Midpoint methodology.

5.4.5 Environmental profile of the TP bio-adhesive

The characterization results obtained for tannin-paraformaldehyde bio-adhesive showed that energy requirements are the main hotspots of the production process (**Figure 11**), reaching contribution values above 50% in the global impact categories.

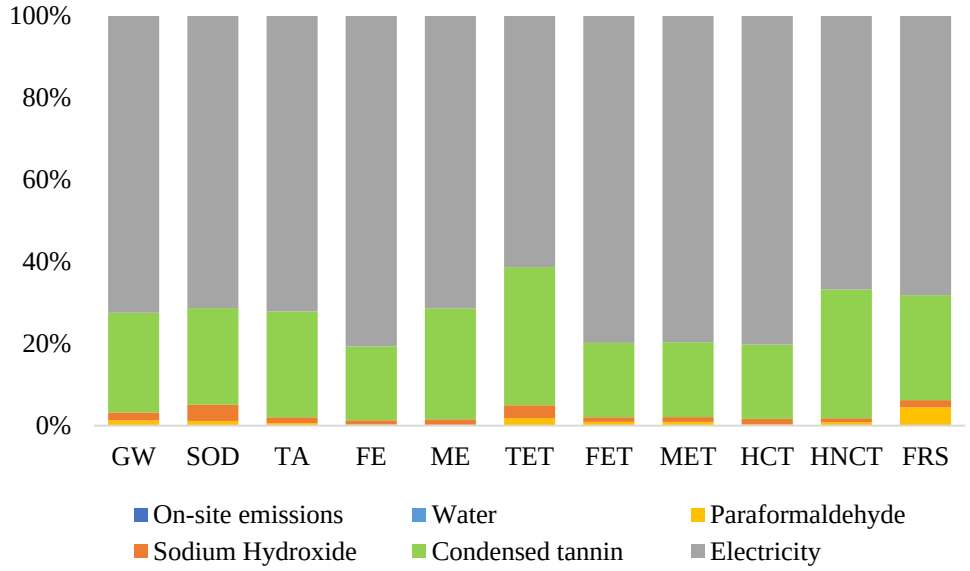

Figure 11. Environmental profile and individual contributions of the TP bio-adhesive considering the Recipe Midpoint methodology.

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Although electricity requirements are the main contributor to the environmental impacts associated with the production of these types of adhesives, it was noted that the

use of tannins in the formulation of bio-adhesives also plays a key role in the environmental profile. This contribution stems from the background activities associated, which also show remarkable energy requirements (**Figure 12**).

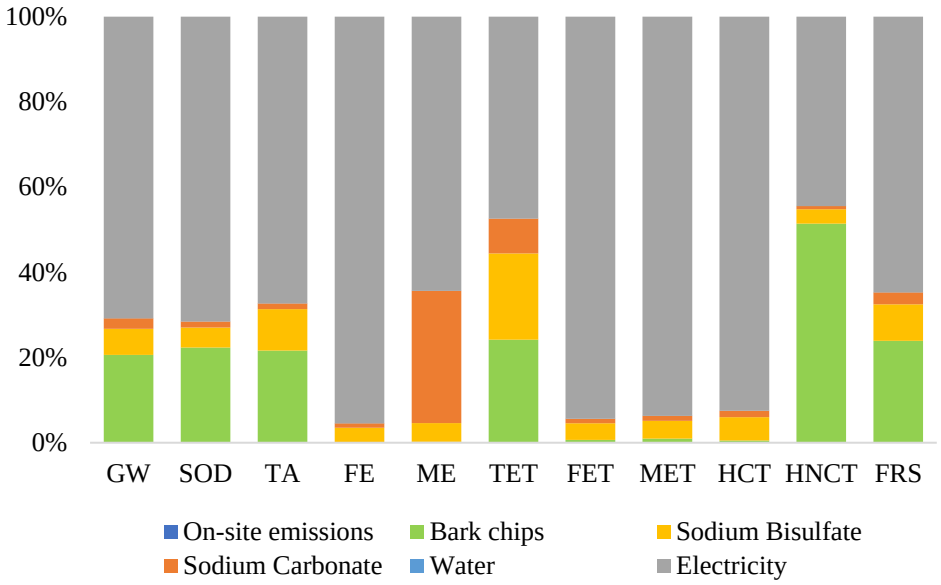

Figure 12. Environmental profile and individual contributions of the tannin condensation stage considering the Recipe Midpoint methodology.

To this end it could be determined that, according to the environmental contribution and profile obtained, the use of paraformaldehyde do not contribute significantly, being the energy requirements and the condensed tannin the main hotspots of this bio-based alternative.

5.4.6 Environmental profile of the TG bio-adhesive

Similar to the previous formulation, electricity production is the main hot spot in the whole environmental profile associated with this type of adhesive, with a noteworthy contribution from condensed tannins (**Figure 13**).

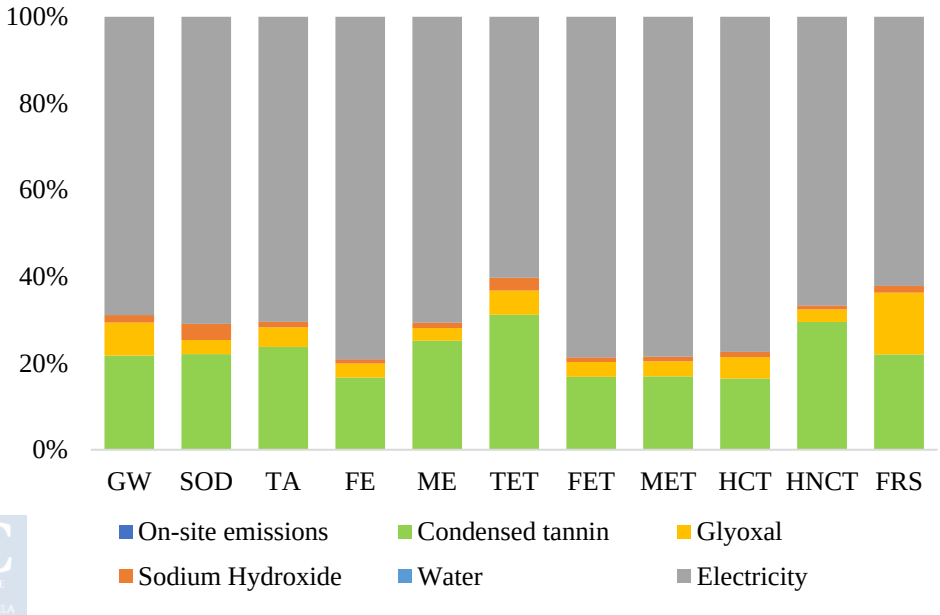

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Figure 13. Environmental profile and individual contributions of the TG bio-adhesive considering the Recipe Midpoint methodology.

In this case, the contribution from the chemical used as a cross-linker for the bio-adhesive production, i.e., glyoxal, is slightly higher than the one achieved by the paraformaldehyde for the categories of GW and FRS 8% and 14% respectively. On the other hand, it is important to point out that the formulation of the paraformaldehyde tannin bio-adhesive is different from that of glyoxal. The amount of crosslinker used for the paraformaldehyde tannin bio-adhesive is half that of the glyoxal tannin bio-adhesive, while derives on a lower contribution of the chemicals in the environmental profile. Given this fact, it could be considered that formulating a bio-adhesive with a higher percentage of bio-based resource and a lower chemical content is recommended.

5.4.7 Environmental profile of the TH bio-adhesive

In the case of tannin-hexamine bio- adhesives, the production of energy requirements is once again the main hotspot, together with the contribution derived from the production of condensed tannins. As can be observed in **Figure 14,** the contribution of hexamine on the category of marine eutrophication is significant. This contribution is associated with the fact that, when hexamine is introduced into the aquatic environment, it is hydrolytically degraded into ammonium and formaldehyde, leading to eutrophication associated with algal blooms. On the other hand, a certain contribution of hexamine is also observed in the TET category. It can be identified as a cause of this contribution that, from the aqueous phase, ammonium can be transferred to the soil and transformed into nitrite and nitrate by the action of nitrifying bacteria present in the soil.

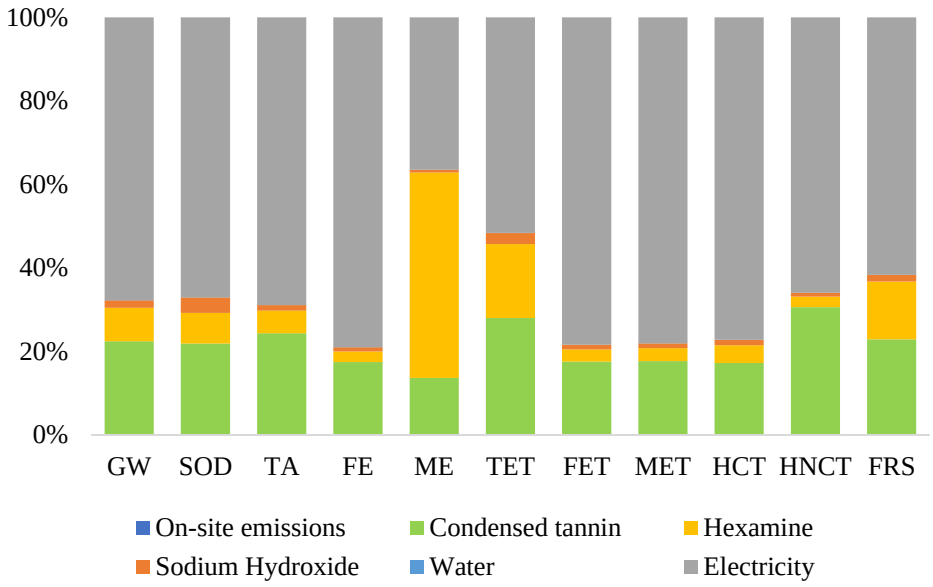

Figure 14. Environmental profile and individual contributions of the TH bio-adhesive considering the Recipe Midpoint methodology.

5.4.8 Environmental profile of the TNA bio-adhesive

The environmental impacts of the tannin-NIPU-ammonium hydroxide bio-adhesive are shown in **Figure 15.** It can be observed that the environmental contribution from the production of dimethylcarbonate (DMC) is the main hot spot in the profile of the global system, with a share of more than 50% in all impact categories. Its lowest contribution is

in TET, where the production of ammonium hydroxide required for the formulation represents a significant impact.

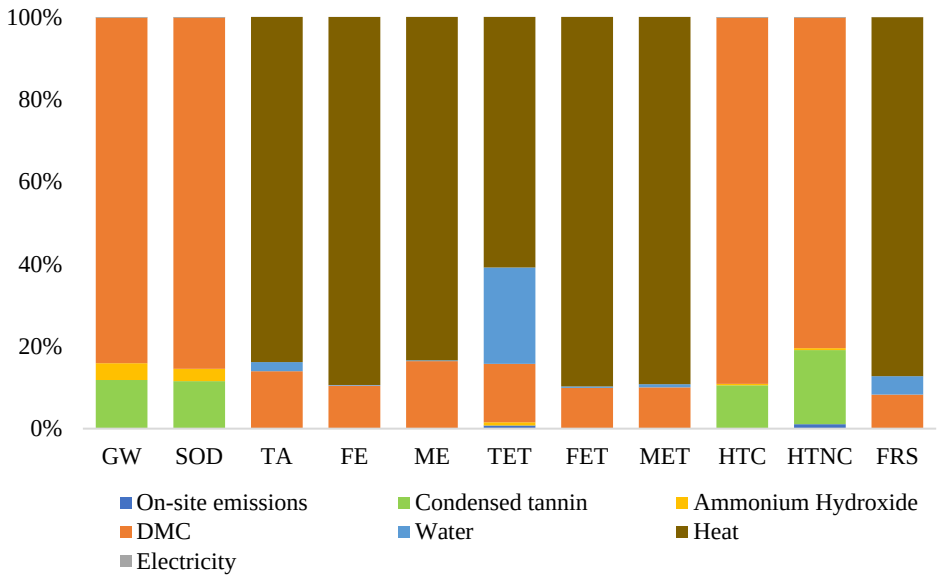

Figure 15. Environmental profile and individual contributions of the TNA bio-adhesive considering the Recipe Midpoint methodology.

With regard to the impact of DMC, its production process based on the oxidative carbonation of methanol has as its main limitation the high energy demand of the process (Garcia-Herrero et al., 2016), with electricity being the most determining factor in all impact categories, except for the FRS category, where carbon monoxide and methanol also represents a significant contribution (**Figure 16**).

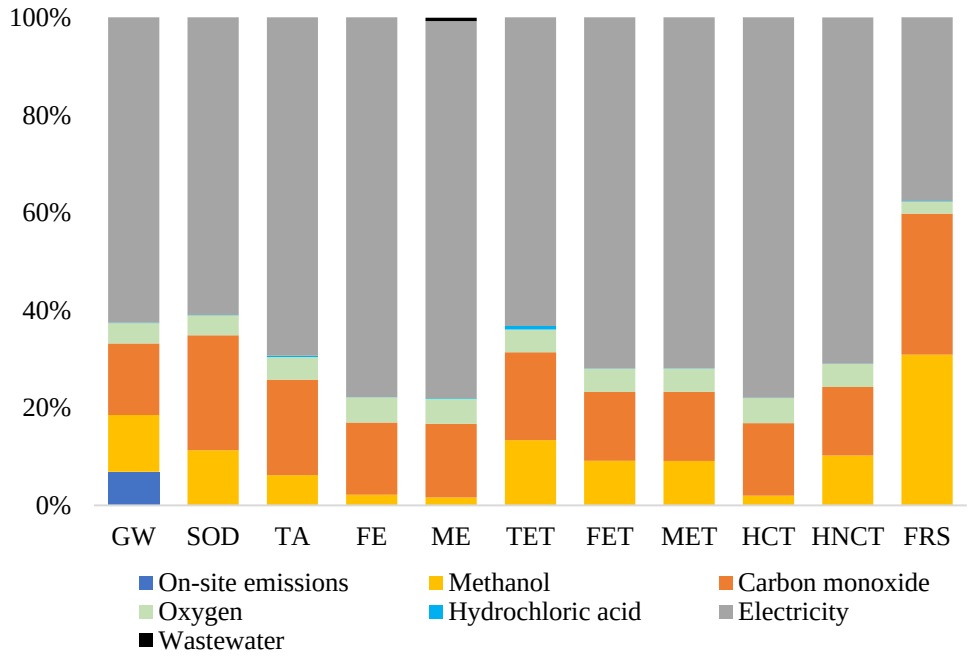

Figure 16. Environmental profile and individual contributions of the DMC crosslinker considering the Recipe Midpoint methodology.

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Methanol is included in the EPA list of 188 Air Toxics, which could contribute to the formation of smog and subsequently, to the impact categories related to ecotoxicity (**Figure 16)**. On the other hand, although it is not considered a toxic compound for the aquatic environment, its biodegradation can lead to oxygen depletion in the water, which could be harmful to aquatic species. In the case of carbon monoxide (CO), its contribution is significant compared to methanol. The environmental contribution of this compound to the ecotoxicity and acidification impact categories is the result of the different chemical reactions that take place at the atmospheric level, especially its oxidation to CO_2 and O_3, both considered greenhouse gases.

5.4.9 Environmental profile of the TNH bio-adhesive

The environmental impact results (**Figure 17**) showed that the use of chemicals in the formulation of the adhesive is the main cause of impacts in all the Midpoint categories. The reason for the environmental contribution of the DMC is analogous to the one just mentioned in the previous section: the high energy demand of the process. This chemical contributes more to the categories of FA, ME, FET and MET where, for the other categories, HDMA is the fossil-based raw material with the large environmental contribution. The reaction of butadiene with hydrogen cyanide is the most extended manufacturing process to produce HDMA. This reaction gives rise to an intermediate product, adiponitrile (ADN), which is converted to hexamethylenediamine by hydrogenation. The by-products and waste streams are amines, CO_2 and imines (mainly hexamethylenimine). In order to perform HDMA environmental profile, a mass-allocation approach has been considered to assign the impacts derived from HDMA production process between HDMA and other co-products (Heavy amines and imines).

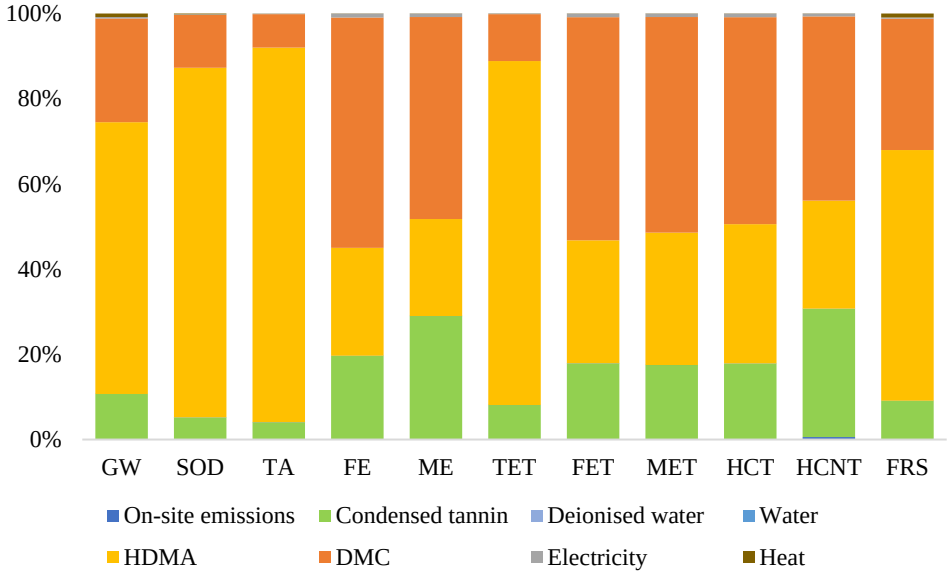

Figure 17. Environmental profile and individual contributions of the TNH bio-adhesive considering the Recipe Midpoint methodology.

In the case of the environmental assessment of HDMA, as can be seen in **Figure 18**, although electricity has a fairly large contribution in certain categories, the most significant energy-related contributor is that of steam, particularly in the SOD and TA categories, where a greater environmental contribution of this compound is identified, with values close to 90% for both categories. The reason for this high contribution derives from the emissions associated with methane production. In addition, in categories such as GWP, FE, ME, MET and FET, its percentage contribution is also high, with values of

27%, 24%, 22%, 22% and 20%, respectively. The main causes are the energy requirements of the HDMA production process, and the emissions associated with the consumption of methane. On the other hand, in the TET category, the environmental contribution is essentially based on the energy demand for HDMA production process.

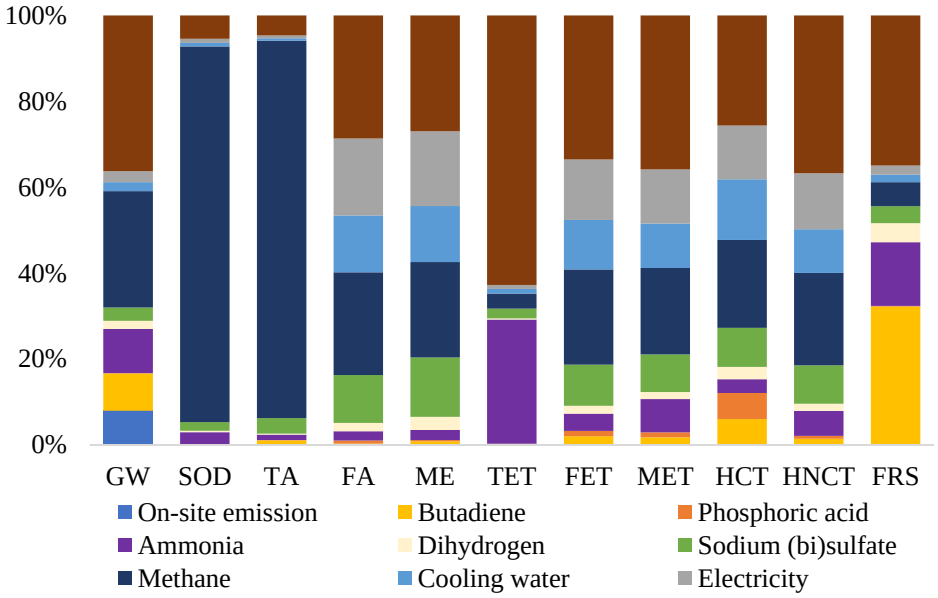

Figure 18. Environmental profile and individual contributions of the HDMA production stage considering the Recipe Midpoint methodology.

5.5 Sensitivity analysis for the alternative bio-adhesives

Once the main manufacturing process bottlenecks associated with bio-adhesives were identified, alternative formulation routes and sensitivity analyses were developed to determine the degree of potential improvement in environmental profiles.

5.5.1 Improved alternative scenarios for lignin-based bio-adhesives.

In the evaluation of the environmental profiles of lignin-based bio-adhesives, it has been observed that the main hotspots are those associated with the energy consumption of the process and with certain crosslinkers used for the formulation of the bio-adhesive. Accordingly, the sensitivity analyses proposed below have been focused on the basis of the results previously obtained, and the following improvements have been proposed:

(1) In the case of NIPU-based adhesives (OSL-NIPU and KL-NIPU), the reduction of the HDMA dose used by 20% has been targeted, given its environmental contribution in most of the impact categories, standing out over the categories associated with eutrophication and ecotoxicity. In addition, the implication of electricity consumption is also notorious, so it has been proposed to evaluate the reduction of its requirement by 25%, as a first sensitivity scenario, as well as to maintain its input values but modifying the source, i.e., instead of using fossil fuels, using renewable energy.

(2) In the case of adhesives formulated from lignin activation by the glyoxalation method, a similar analysis to the previous one has been proposed, with the difference that, since electricity is the main hotspot in the lignin activation process. The optimization scenarios are analogous: reducing electricity use by 25% and maintaining the electricity requirement but using renewable resources. Additionally, the reduction of the crosslinking agents used in the bio-adhesive formulation has also been evaluated, in a range of 20%, PEI for the case of the bio-adhesive formulated with Kraft lignin and

furfural for the one formulated with Organosolv lignin. Once the sensitivity scenarios have been proposed for the conflicting variables of the environmental profiles, the impact reduction results are integrated in **Figure 19**.

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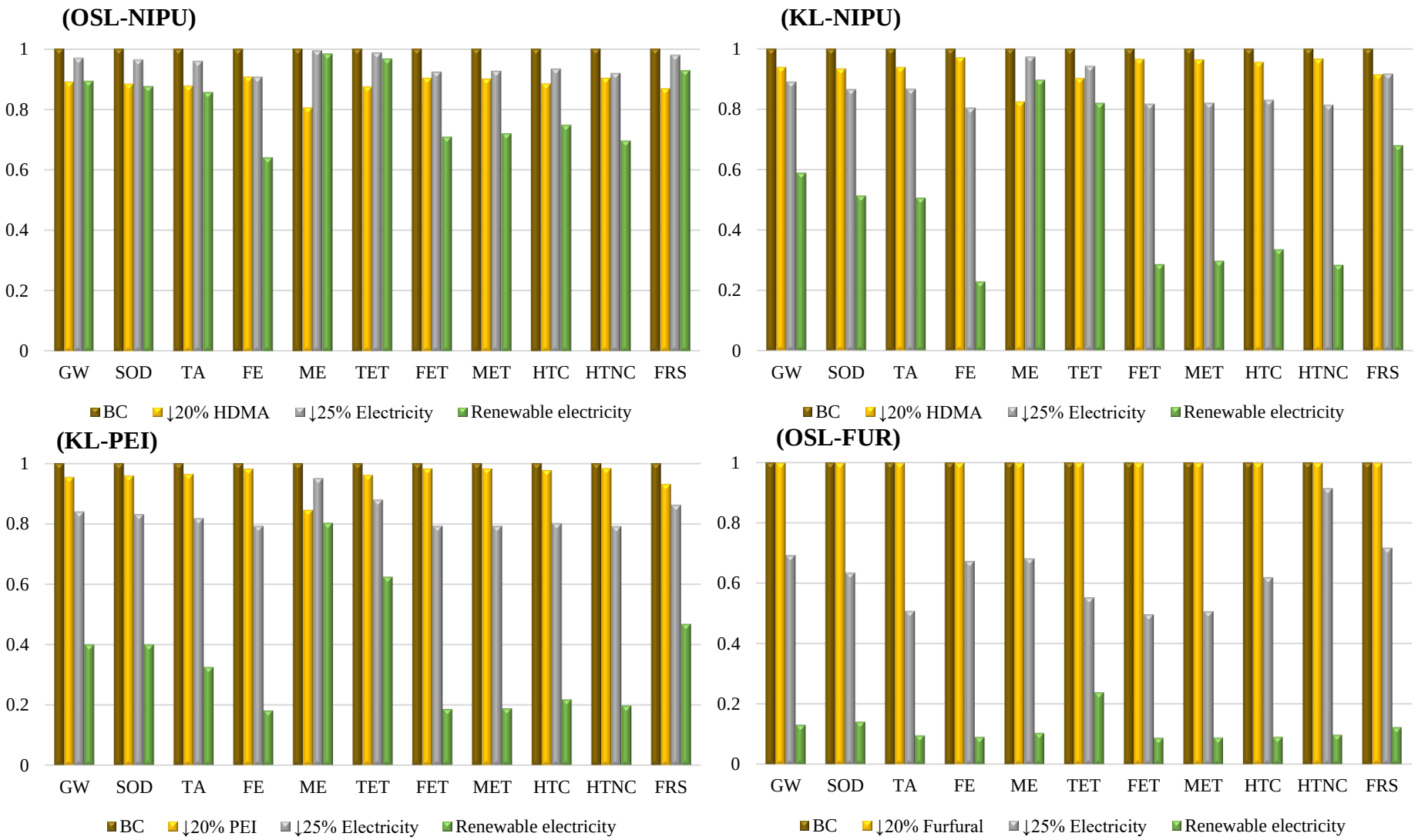

Figure 19. Sensitivity scenarios for lignin-based bio-adhesives.

In the case of the OSL-NIPU bio-adhesive, it is observed that the greatest optimization of the scenario is achieved when electricity from renewable energies is used, with environmental impact reduction ranges from 2% for the ME category to 36% for the FE category, reaching an average reduction in the set of categories of around 18%. However, the modification of the dose of HDMA used is also an important aspect that significantly influences the environmental profile obtained, achieving an impact reduction of between 9% for the HTNC category and 13% for the consumption of fossil resources, FRS, with an average reduction of 12%

Regarding the KL-NIPU adhesive, the improvement alternatives are analogous to the previous bio-adhesive, although more significant improvement values have been achieved, given the greater amount of electricity required for this bio-adhesive scenario. Again, the use of renewable resources is stated as the most viable option from a sustainability point of view, with the sole exception of the ME impact category, where the commitment to reduce the dose of HDMA implies a greater reduction in impact. As for the numerical reduction values, for the case of variation in the use of the crosslinking agent, values in the order of 3% have been obtained for the FE and HTNC categories, and 18% for the ME category. As for the reduction of electricity consumption, the average reduction reaches a value of 13%, while the use of renewables increases the reduction of the impact to 51%, with a range of improvement from 10% for the ME category to 77% for the FE category.

For the KL-NIPU and OSL-FUR bio-adhesives the energetic implication is higher compared to the previous ones, given the selection of glyoxylation for lignin activation. The process time, as well as the requirements of maintaining a homogeneous reaction medium, imply a high consumption of electrical energy in this first pre-treatment stage. This is why a great improvement in the environmental profile obtained is observed when opting for a 25% reduction in electricity consumption, as well as for energy renewability, the reduction being greater when the latter alternative is considered. On the other hand, the reduction of the dose of the crosslinking agent used has also been evaluated. For the case of the KL bio-adhesive a 20% reduction of PEI dose, while for the case of the OSL bio-adhesive, a 20% reduction value of furfural.

In the evaluation of the KL-PEI bio-adhesive, it is observed that the range of reduction achieved when evaluating the use of renewable electricity is between 20% for the ME category and 82% for the FE category, reaching an average reduction of 64%, which is reduced to 17% when evaluating the reduction of electricity needs by 25%. On the other hand, the variation of the impact achieved with the reduction of the PEI dose in the ME category stands out, reaching 15% with respect to the base scenario, although the average reduction is only 4%.

Finally, with respect to the OSL-FUR bio-adhesive, it can be stated that the reduction in environmental impact due to the modification of the furfural dosage is unimportant in all impact categories, although it is very significant in the case of the electrical resource assessment. The range of improvement when using renewable energies is between 76% for the TET category and 91% for the FE, FET, MET and HTC categories, with an average reduction amounting to 88%, being then the scenario that achieves the greatest improvement in the environmental profile. However, when the 25% reduction in electricity requirements is assessed, the average reduction drops to 36%, with the greatest improvement in the impact value being achieved in the FET category, with a 50% reduction.

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5.5.2 Improved alternative scenarios for tannin-based bio-adhesives.

In the case of glyoxal tannin, paraformaldehyde and hexamine bio-adhesives, energy requirements are the main cause of the high environmental impact. Therefore, a sensitivity analysis focuses on reducing the amount of electricity needed for the process: up to a 25% reduction in the different scenarios. This option of sensitivity analysis is proposed as a way to improve the production process for the formulation of bio-adhesives, since in the modeling of the process proposed for this study, the option of energy optimization has not been modeled, that is, the use of the hot and cold streams available to reduce energy resources or even require more energy efficient equipment. Thus, the possibility of reducing energy consumption by 25% is considered a viable option.

On the other hand, in the case of tannin-NIPU based resins, the following alternatives are presented:

(1) A 20% reduction in the DMC dosage used in the tannin-NIPU formulation with ammonium hydroxide bio-adhesive has been assumed as an improvement option.
(2) Substitution of DMC by ethylene carbonate (EC). Both compounds are carbonate esters, their main difference being that DMC has a linear molecular structure, in contrast to EC which is a cyclic molecule. However, ethylene carbonate is also used as a precursor for the synthesis of polymeric urethanes (NIPU) (Kathalewar et al., 2013), following a polycondensation route by the reaction of EC with amines, in this case, with HDMA or ammonium hydroxide (Datta and Włoch, 2016). Thus, the possibility of substituting DMC for EC in the formulation of NIPU bio-adhesives could be an alternative to the process, so a sensitivity analysis was performed. The same bio-adhesive production yield was assumed regardless of the chemical used.
(3) A 20% reduction of the HDMA dose used in the case of tannin-NIPU with HDMA bio-adhesive. Considering the reduction in DMC requirements, the same approach has been adopted in HDMA consumption.

The assumption of wood bark for tannin extraction as a waste from wood manufacturing processes has been considered for all proposed bio-adhesive alternatives. This consideration can be proposed based on the amount of wood waste generated annually. Based on data available in the USDA Forest Service report, approximately 58% of the total wood used for the manufacture of wood products is managed as waste, including sawdust and coarse residues, among others (Falk and McKeever, 2012). These residues could be recovered or used for energy production, for the manufacture of lower quality panels or for the production of other bio-based products, such as bio-adhesives for wood panels. **Figure 20** shows the overall normalized scores obtained for the proposed sensitivity analysis for bio- adhesives. A more detailed analysis of the results is provided below.

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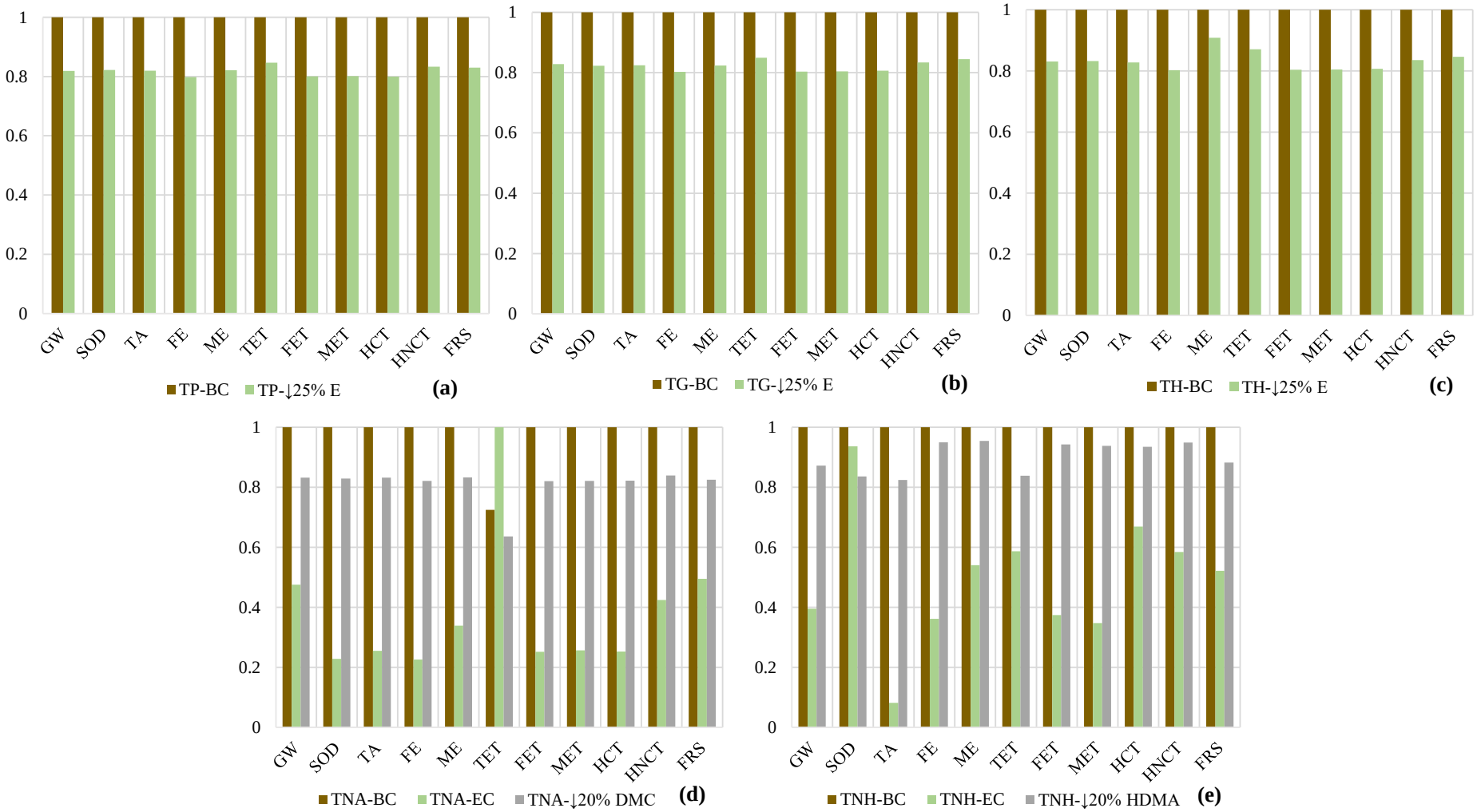

Figure 20. Normalized sensitivity scores obtained for the tannin bio-adhesive scenarios: (a) TP, (b) TG, (c) TH, (d) TNA and (e) TNH bio-adhesives.

Variations in environmental impacts are observed in the scenarios for the TP, TG and TH bio-adhesives due to the reduction of 25% in energy demand. The categories with a better environmental result after the sensitivity analysis are nearly the same for the three adhesives. In the case of GWP, the greatest reduction in impact is achieved by the tannin-paraformaldehyde bio-adhesive, with a percentage reduction of 18% compared to the base case. For the glyoxal and hexamine-based bio-adhesives, a value of 17% reduction is obtained. For the FE category, the percentage reduction obtained for the tannin-paraformaldehyde bio-adhesive amounts to a 20% that, with the HCT, is the impact category with which the higher reduction is obtained. In the case of tannin-glyoxal, the higher percentage of reduction is also 20% for the impact categories of FE, FET, MET and HCT, while the HNCT and FRS are the ones that achieved lower improvements, 16.7 and 15.5%, respectively.

In the case of the tannin-hexamine alternative, the values of reduction achieved are similar to that of tannin-glyoxal bio-adhesive: 20% as the maximum reduced percentage value for the impact categories of FE, FET, MET and HCT, but the lower value of reduction obtained for the ME impact category, with the reduction of 9% in the environmental load.

As examined above, in the case of the tannin-NIPU with the ammonium hydroxide bio-adhesive, the environmental contribution of DMC was very significant for most impact categories, so the reduction in its dose and its substitution by EC is expected to provide significantly better environmental results. By reducing the dose of DMC by 20%, improvements of up to 18% were achieved in the FA, MET and FET categories. With the chemical modification alternative, the improvement is comprehensive, with the exception of the TET category, where no change from the base case study is observed.

Figure 20 also shows how the environmental profile of tannin-NIPU with HDMA bio-adhesives improves with the 20% reduction of HDMA dosage, as well as with the substitution of DMC for EC. In the case of 20% reduction of the DMA dose, the reduction of impacts is evident in all impact categories, being more noticeable in the TA, TET and SOD categories, with impact values between 16-18% lower. However, the possibility of replacing DMC by EC seems to be a much more suitable option from the environmental point of view, reaching reduction values above 40% for the categories of FA (49%), ME (40%), FET (47%) and MET (46%).

Finally, in the case of considering wood bark as a waste stream for tannin extraction, the results show some improvement in some impact categories, but much less pronounced compared to the previous results. The greatest improvement in the environmental profile is observed in the case of bio-adhesives based on EC and ammonium hydroxide. Specifically, GWP, SOD and TA categories find reductions in environmental impact of 7%, 15% and 13%, respectively.

5.6 Comparison between base case scenarios

The designation "bio" does not always guarantee that the environmental impacts associated with adhesive production processes are less than the reference processes, considering that these are typically processes with a higher degree of development and optimization than those at an earlier stage of development. Therefore, it is of special interest to compare the different bio-adhesive alternatives with the most used adhesives based on urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF). The inventory data for the background processes of these synthetic adhesives have been taken from Ecoinvent® data-base version 3.8 (UF and PF) and Silva et al. (2015) for the MUF (Silva et al., 2015). With this objective, the Recipe Endpoint

calculation method has been applied, through which a single environmental value is obtained for each of the proposed adhesives. The endpoint indicators used for the analysis are: Human Health (HH), Ecosystem Quality (EQ) and Resource Scarcity (RS).

In the case of tannin bio-adhesives, the values obtained in the endpoint indicators are promising and may be potential candidates to substitute petrochemical-based adhesives. In the case of the Human Health (HH) category, they perform better than phenol-formaldehyde resin (**Figure 21**), and similar to urea-formaldehyde resin. When evaluating the EQ damage category, the values obtained for the tannin bio-based adhesive are slightly higher to that of formaldehyde-based resins, being TP the alternative with the lowest value (**Figure 22**). It is important to note that in the FRS category (**Figure 23**), which includes both mineral and fossil resources, the values obtained are considerably better for renewable-based adhesives compared to synthetic ones. As regards the overall value obtained after the normalization stage, it is observed that the base cases of tannin-formaldehyde, tannin-glyoxal and tannin-hexamine adhesives are better from the environmental point of view compared to phenol-formaldehyde resin, with results also very close to those obtained for urea-formaldehyde resin.

In the case of lignin bio-adhesives, the results obtained are also interesting from the point of view of an environmental perspective. Specifically, evaluating the HH damage category, the OSL-NIPU alternative is the one with a score with a lower value when compared to non-renewable based resins, being the glyoxalated bio-based adhesives, both KL and OSL, the ones with the worst HH value, significantly higher to that of fossil-based resins (**Figure 21**).

Considering the EQ category, the values obtained are slightly higher than those of synthetic adhesives, for the case of OSL and KL-NIPU bio-based adhesives (**Figure 22**). The use of chemical compounds (ammonium hydroxide and HDMA) for the formulation of adhesives is the main factor affecting this category. In addition, the use of DMC to obtain NIPU also has a high contribution to this value, derived from the energy dependence of its production process. It is also important to mention that the bio-adhesives formulated with non-isocyanate polyurethanes is advisable, since petrochemical polyurethanes use phosgene in their production process, whose levels of toxicity and environmental impact would be much higher. Lastly, the scores obtained on the category of RS, those are promising for all the lignin-based alternative scenarios under assessment, as all of them have a reduced, or equal, value to that of PF fossil resin, being the OSL-NIPU alternative the one that achieved a lower score, similar to that of UF and MUF resins (**Figure 23**).

Bearing all this in mind, it could be considered that all the tannin-based bio-adhesives proposed scenarios could be considered as promising alternatives since the values for bio-adhesives obtained on the EndPoint scores are similar or lower when both of them are compared. With respect to the lignin-based alternatives, only the one of OSL-NIPU achieve damage category scores in line with synthetic resins, thus being the most adequate alternative from the environmental perspective. On the other hand, it has been demonstrated that the glyoxalation step for lignin functionalization is a highly impactful step that implies a huge contribution over the overall environmental profile. To this end, it could be concluded that opting for another activation procedure, such as that developed in NIPU-based bio-adhesives, should be the preferred one and activation with glyoxal should be either avoided or improved in order to reduce its associated environmental burdens.

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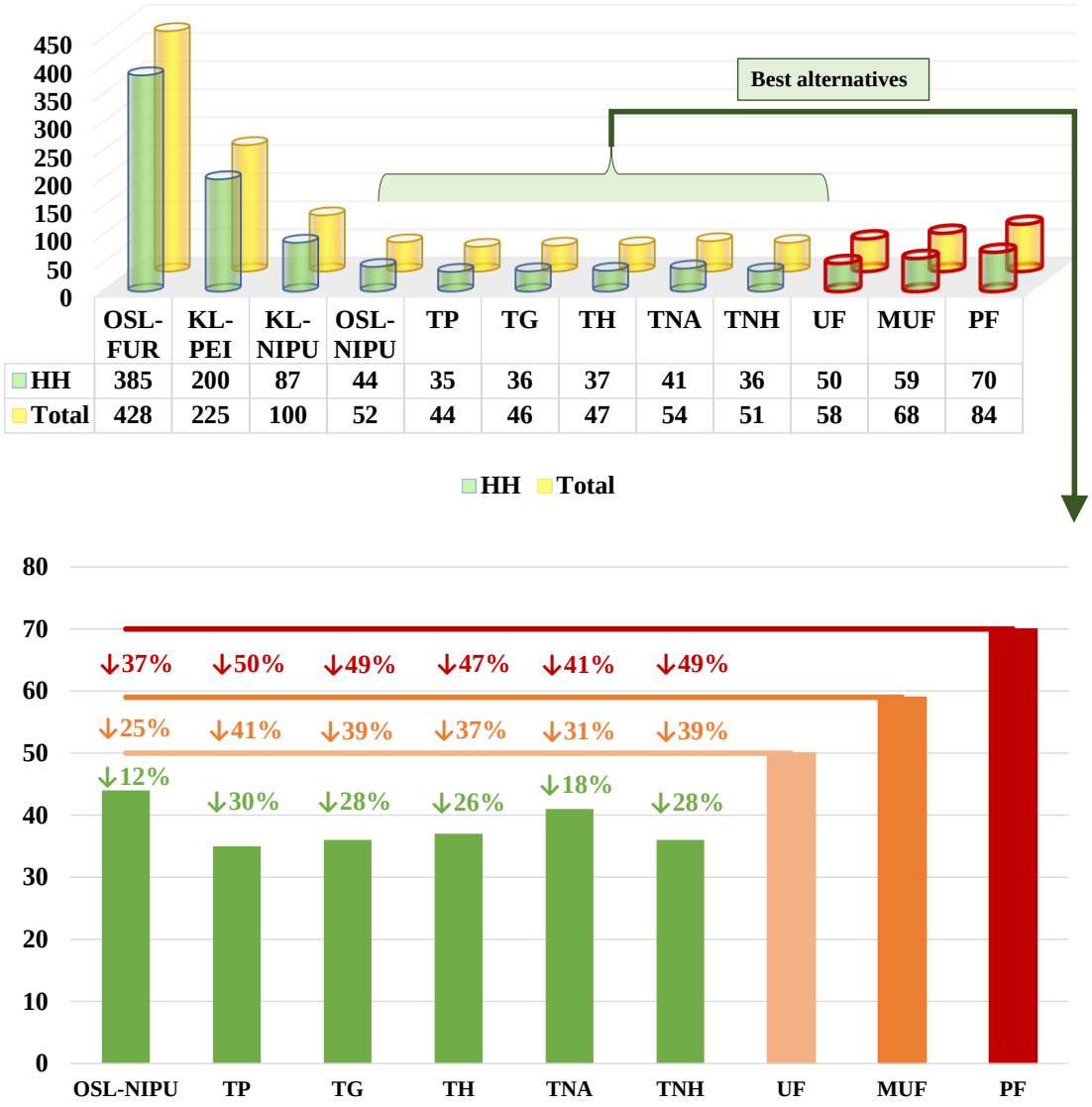

Figure 21. Human health (HH) and total EndPoint single scores obtained for both bio-based and synthetic resins.

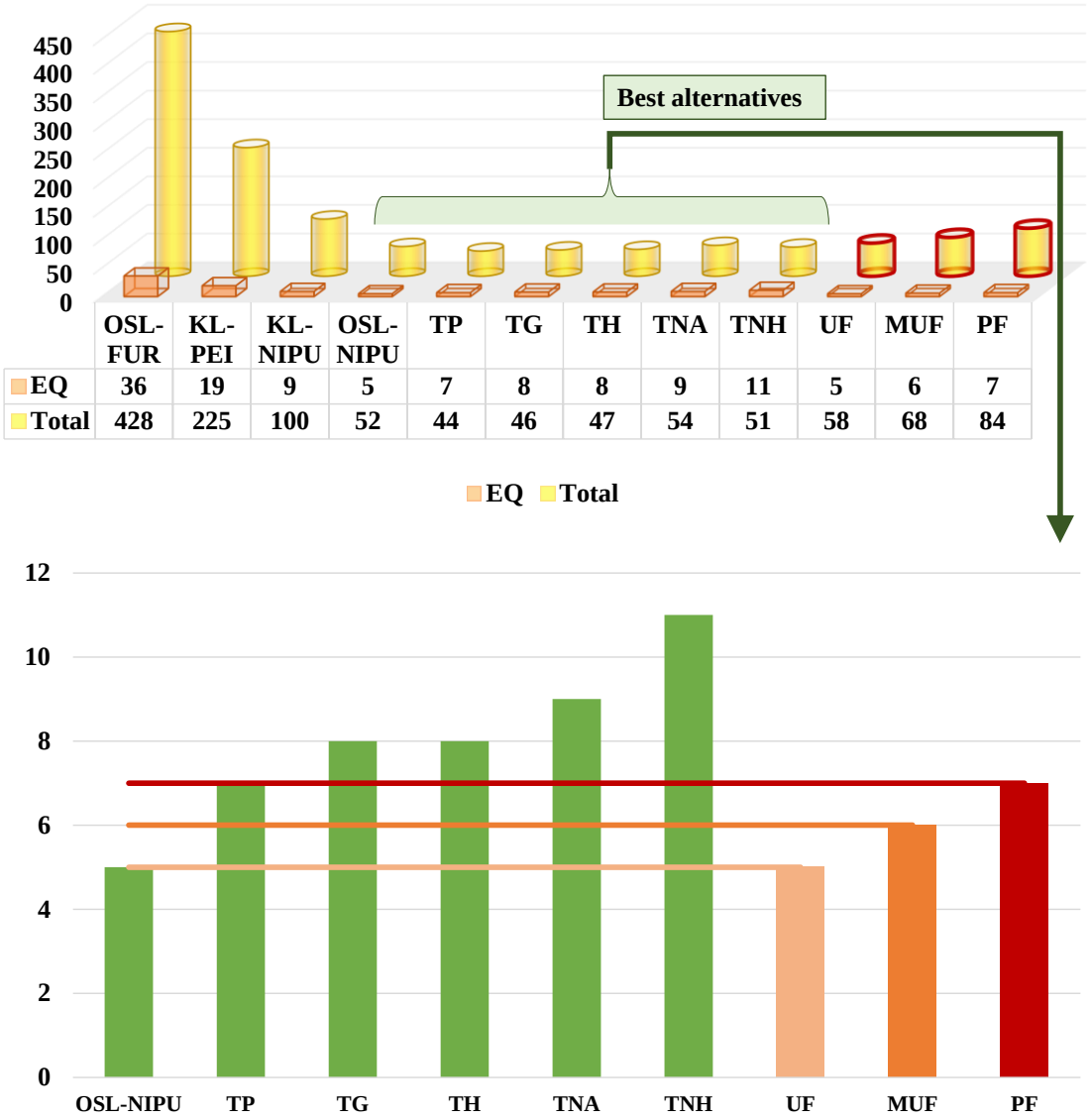

Figure 22. Ecosystem quality (EQ) and total EndPoint single scores obtained for both bio-based and synthetic resins.

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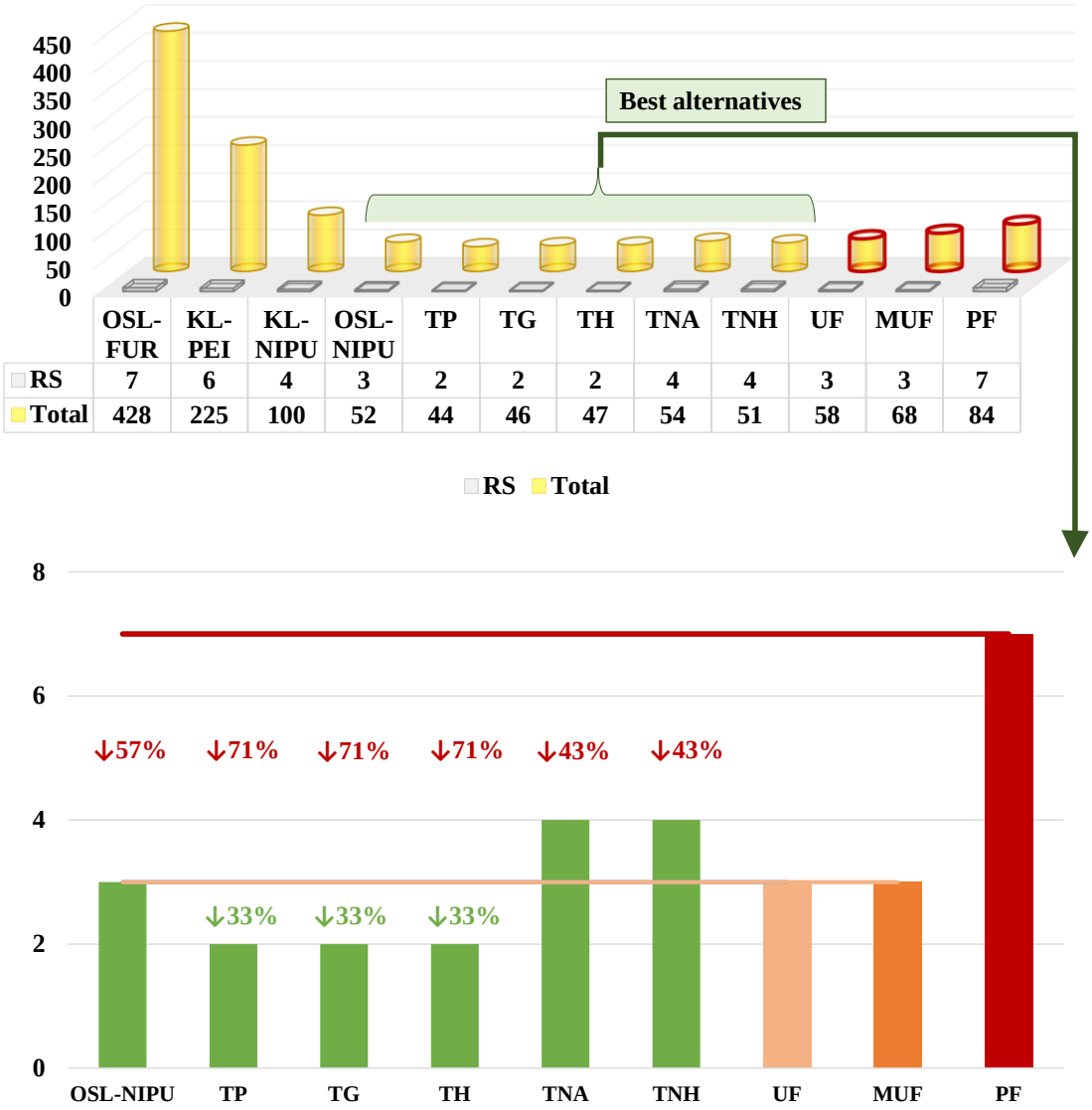

Figure 23. Resource scarcity (RS) and total EndPoint single scores obtained for both bio-based and synthetic resins.

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5.7 Conclusion remarks

In this chapter, an environmental evaluation of lignin- and tannin-based bio-adhesives has been developed, considering four different scenarios for lignin and five for tannins, including also a comparison with the most commonly used synthetic resins. The results show that tannin-based bio-adhesives are a good option to substitute synthetic resins used in the wood-based panel industry. From the point of view of resource scarcity, all options present lower impact results than synthetic resins, and from the perspective of the other damage categories, the results are analogous to those of formaldehyde-based resins. On the other hand, by evaluating the contribution of the chemicals used in their formulations, such as glyoxal, hexamine, ammonium and HDMA, although their environmental contribution values are not very significant, seeking to improve the environmental quality of adhesives, it would be advisable to think on using more sustainable options. The last point to be remarked is the energy requirements of the production processes which, in most of the cases explored, are the main contributors to environmental impacts, so an improvement in energy efficiency would be necessary to reduce their negative effects on the environment.

In the case of lignin-based bio-adhesives, the results are not as promising as in the case of tannins, with only the OSL-NIPU alternative achieving results similar to those of synthetic resins, thus having the potential to serve as an alternative to formaldehyde-based adhesive. As discussed in previous sections, the activation of lignin to make it suitable for bio-adhesive formulation is the main bottleneck in process formulation and environmental contribution, with the glyoxalation procedure being the worst option from an environmental perspective, given its high energy demand. In this sense, an improvement in the lignin activation step is necessary to improve the environmental profile of lignin-based scenarios.

As a general conclusion, it could be stated that tannin-based bio-adhesives are the most recommended options, together with the bio-based alternative OSL-NIPU. However, further research is needed to improve their technical manufacturing performance and energy efficiency. The results obtained in this chapter could be considered as a starting point in the evaluation of the environmental sustainability of tannin- and lignin-based natural adhesive production systems, as most of the results show that they are very viable and sustainable options for use in the wood-based panel industry.

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6

Agri-food industry by-products as feedstock for bio-adhesives

This chapter partially reproduces content already published as "Arias, A., Feijoo, G., Moreira, M. T. (2021). Evaluation of starch as an environmental-friendly bioresource for the development of wood bioadhesives. *Molecules*, *26*(15), 4526", "Arias, A., González-García, S., Feijoo, G., Moreira, M. T. (2021). Environmental benefits of soy-based bio-adhesives as an alternative to formaldehyde-based options. *Environmental Science and Pollution Research*, *28*(23), 29781-29794" and "Arias, A., González-García, S., González-Rodríguez, S., Feijoo, G., Moreira, M. T. (2020). Cradle-to-gate Life Cycle Assessment of bio-adhesives for the wood panel industry. A comparison with petrochemical alternatives. *Science of The Total Environment*, *738*, 140357."

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SUMMARY

Research in the field of resins with lower environmental impact is not only limited to those based on lignin or tannins. Considering as a starting condition the search for renewable raw materials, there is a growing interest in the environmental evaluation of different adhesive alternatives based on soybean and starch, as potential options to be used as wood bio-adhesives.

The rationale behind the interest of using those bio-based resources for wood adhesives production is their low purchase cost, their huge availability, their easy-to-handle property for bio-adhesives formulation and their similar characteristics and properties of adhesion when compared to synthetic resins. In **Chapter 6** a total of ten bio-based adhesives scenarios are developed, six for soy, considering the direct use of soybean meal and the extraction its protein content for bio-adhesive formulation, and four for starch, whose activation has been developed following two different approaches: hydroxylation and oxidation.

In order to assess its potentiality over the formaldehyde-based resins, an environmental assessment following the LCA methodology was developed, considering also the evaluation of alternative scenarios for improving its environmental profiles. Both ReCiPe MidPoint and EndPoint methods were used for evaluating and comparing the alternatives, with the aim of selecting the most promising bio-based scenario to substitute formaldehyde resins.

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6.1 Recovering agri-food residues to wood bio-adhesives production

One of the options being considered to develop adhesives with lower environmental impact is based on the partial or total substitution of formaldehyde by formulating bio-adhesives based on plant proteins (Kajaks et al., 2012). The techno-economic feasibility of this type of bio-adhesives must ensure that a number of requirements are met; similar performance to synthetic alternatives, adequate strength and stiffness properties according to standards and competitive cost (Frihart and Birkeland, 2014). In addition, it is anticipated that the use of bio-adhesives could lead to a number of environmental credits, especially in terms of fossil resource depletion and associated CO_2 emissions. Despite the promising benefits of bio-based adhesives, an unbiased holistic perspective must be conducted, so that all environmental aspects related to the process are addressed; especially if the impact categories linked to energy consumption of a process that has not been optimized or also land use for biomass cultivation are considered.

Soybean is a renewable resource with favorable characteristics for use as a raw material in the manufacture of bio-adhesives, namely, abundance, ease of processing and low cost (Vnučec et al., 2017). Its derivatives, including soy protein (SPI), defatted soybean meal (DSF) and soybean meal (SF) are ideal materials for the production of bio-adhesives. Although soy protein has high protein purity, with levels above 90% crude protein (Hojilla-Evangelista and Evangelista, 2009), the transition to an industrial-scale process has been significantly limited due to its high cost. Recent research related to soybean-based adhesives has been mainly directed to the modification of soybean meal fractions. Performance analysis of soy-based bioadhesives shows acceptable but not excellent water resistance, which may be a disadvantage compared to well-established alternatives of petrochemical origin (Lei et al., 2014). To address these limitations, it is considered that the addition of crosslinking agents can improve adhesive performance (Ferdosian et al., 2017a). Bearing this in mind, the optimization of the use of crosslinking agents and the adaptation of the process operating conditions are key aspects to improve the environmental, technical and economic profiles of the bio-adhesives.

In addition to soybean, another alternative renewable raw material for the development of wood bio-adhesives, considered as an option of special interest is starch. In particular, starch is the second most abundant lignocellulosic polymer in nature (Gadhave et al., 2017). Moreover, it is a low-cost and high-potential resource, as it is biodegradable. However, despite these advantages, its direct use is not feasible for the development of wood bio-adhesives given its content in hydrophilic hydroxyl groups, which derives in low moisture tolerance and high water absorption (Monroy et al., 2019; Yin et al., 2020). Pursuing to bypass this drawback, a pre-treatment step is required, based on the application of suitable operating conditions and crosslinking agents to remove those excessive hydrophilic groups (Gadhave et al., 2017).

The environmental profile of bio-adhesives has been scarcely addressed (Arias et al., 2020; McDevitt and Grigsby, 2014; Yang et al., 2020). Furthermore, comparison between different bio-adhesive options is not straightforward because it will depend on whether the selection of the functional unit, system boundaries and impact assessment methodology are similar. Available reports on bio-adhesives focus on the formulation of the adhesive and its validation for use in the wood processing industry (Ferdosian et al., 2017b). In this context, this chapter aims to provide essential information on the different alternatives for soy- and starch-based adhesives for which no environmental studies have been performed. For this purpose, due to the lack of industrial-scale production data, it is necessary to develop mass and energy balances needed in the process simulation using the Aspen Hysys® tool. The conceptual process design is essential to provide the key

inventory data for the production process, not only for raw materials, products and energy, but also for emissions from each stage of the manufacturing process. In order to perform the quantitative analysis of the overall environmental impacts according to the life cycle methodology, looking to be possible to identify real opportunities for competition between a widely tested fossil-based adhesive with a biotechnological alternative that aims to stand out as a more sustainable product, thus promoting the concept of green chemistry (Loste et al., 2020).

6.2 Describing the scenarios under assessment

Looking forward the description of the scenarios, considering a definition of the process schemes and stages required for the bio-adhesive formulation and production, two main sections are included, the one referred to the lignin-based resins and the other based on the tannin bio-adhesives alternatives.

6.2.1 Soy based bio-adhesives.

Six scenarios have been considered for the production of soy-based bio-adhesives (**Table 12**).

Table 12. Scenarios of soy-based bio-adhesives under assessment

Soy bio-adhesive	Acronym	Justification
Soybean meal with dicyandiamide as cross-linker	SF + D	Simplicity in the bio-adhesive production route, which could lead to less environmental impact
Soybean meal cross-linked with waterborne polyurethane	SF + WP	Bio-adhesive with better mechanical properties and higher water resistance due to the addition of water-based polyurethane
Soybean meal cross-linked with SBDS and epoxy resin	SF + SE	Improvement of the bio-adhesive adhesion properties by the addition of SBDS, which leads to an increase in water resistance and shear strength
Soy protein cross-linked with epoxy resin and polyacrylamide	SP + EP	Mild process conditions which entail lower energy requirements and possibly good environmental profile
Soy protein cross-linked with maleic anhydride	SP + MA	Good bio-adhesive quality due to the strong bonding formations through the grafting step
Soy protein cross-linked with tannin resin	SP + TR	Formulation of the bio-adhesive based on two renewable raw materials (soy protein and tannin)

The importance of adding crosslinkers in the formulation of bio-adhesives correlates with the need to improve the physical-chemical characteristics of the final product, especially in relation to those relevant to the manufacture of wood panels. The crosslinkers used for the formulation of the different soy-based bio-adhesives proposed could be mixed during the adhesive production process or just before its application to the wood board (Lei et al., 2014). It is also feasible in the manufacture of soybean meal and soy protein bio-adhesives (Ghahri et al., 2018). The addition of crosslinkers not only improves the production stage of the board, but also yields the structural quality of the wood board (Wescott et al., 2006) and increases its tolerance to moisture (Pizzi and Ibeh, 2014).

For soybean meal, the Ecoinvent® database has been used for inventory data. According to the data available in the literature on the average production of synthetic resin facilities (Yang and Rosentrater, 2019b), a production capacity of 24 t/d of bioadhesive has been selected for the large-scale simulation.

Two feedstocks have been proposed for the formulation of soy-based bio-adhesives, namely soybean meal and soy protein. Agricultural activities of soybean cultivation, including fertilization and irrigation, are included in the analysis. After harvesting, the soaked soybeans were precooked and dehulled, before being dried, ground and sieved. Soybean meal was used for the SF+D, SF+WP and SF+SE alternatives, while soy protein is used for the SP+EP, SP+MA and SP+TR alternatives. Therefore, the scenarios based on the use of the latter require an additional step within the system boundaries based on the extraction of the protein from the soybean meal. The extraction process is intensive in terms of chemicals and energy requirements and information regarding their performance has been taken from (Berardy et al., 2015). In terms of products, the extraction process results in three co-products: soy protein, whey and spent flour. Consequently, a mass-based allocation has been considered to distribute the environmental burdens among these co-products. For the soybean meal, the Ecoinvent® database has been used for inventory data. According to the data available in the literature on the average production of synthetic resin facilities (Yang and Rosentrater, 2019b), a production capacity of 24 t/d of bio-adhesive has been selected for process modelling at large scale.

6.2.1.1 Soybean meal with dicyandiamide (SF+D) bio-adhesive

According to the procedure proposed by Solt et al. (2019), soybean meal is mixed with water at 35°C for 60 min and then HCl containing 0.01% (w/w) ferric chloride is added to the mixture (Solt et al., 2019b). These three components are mixed for 30 min under constant agitation. After this time, the crosslinking agent dicyandiamide is added and mixed for 60 min. Finally, NaOH is added to adjust the pH of the adhesive. The foreground system data have been estimated by modeling the process in Aspen Hysys®.

6.2.1.2 Soybean meal with waterborne polyurethane (SF+WP) bio-adhesive

One of the main problems related to the use of soy protein-based bio-adhesives is the presence of hydrophilic amino acids in their molecular structure, which has led to poor resistance to moisture. This characteristic could be improved by the use of waterborne polyurethane (WPU) as a cross-linking agent, leading to the production of soy bio-adhesives with improved mechanical properties and higher water/solvent/thermal and abrasion resistance (Hu et al., 2016; Zhang et al., 2012) through the formation of stronger intermolecular interactions with the reactive groups in soybean meal. One of the most commonly used WPUs for the formulation of soybean-based bio-adhesives is called poly-(butylene adipate), a polymer consisting of the monomers adipic acid and 1,4-butylene glycol.

WPU are reactive compounds that form covalent and hydrogen bonds. The cross-linking chemical is added by dispersion into the soybean meal (Liu et al. 2017), so it became necessary to mix the soybean meal with water and pH is adjusted using ethylene glycol, urea and sodium hydroxide. This first mixing is done by constant stirring for 60 min at 80°C (Zhong Wang et al., 2019) (Wrang et al. 2019). Once this slurry is formed, WPU is added to the mixture under constant agitation for 160 min at 76°C to promote the formation of covalent bonds. After this time, the mixture is cooled to room temperature (Wang et al., 2018).

6.2.1.3 Soybean meal with SBDS and epoxy resin (SF+SE) bio-adhesive

The adhesion properties of soy protein are improved with the use of sodium dodecyl benzene sulfonate (SBDS) in terms of increased water resistance and shear strength (Huang and Sun, 2000). The addition of epoxy resin also helps to improve these adhesive properties due to the increased formation of covalent bonds with the reactive groups in soybean meal.

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The formulation of this bio-adhesive requires the reaction of an aqueous solution formed by SDBS, CaO and NaOH with the soybean meal, maintaining constant agitation at 88-92 ºC for 3 h. Epoxy resin (6.5% weight) is added to this slurry, resulting in a 41% improvement in wet shear strength over the adhesive without epoxy resin (Lei et al., 2014).

6.2.1.4 Soy protein crosslinked with epoxy resin and polyacrylamide (SP+EP)

First, it is important to mention that the epoxy resin used as a bio-adhesive crosslinker is a waterborne epoxy resin, which is considered as an effective cross-linking agent for soy bio-adhesives (Luo et al., 2016). The production process involves two process stages, the first of which is the extraction of the soybean protein. The second consists on the addition of the soy protein to water containing 0.05% polyacrylamide for 20 min at 40°C under continuous agitation. The epoxy resin is then added to the mixture, maintaining agitation for 30 min and raising temperature to 45°C (Wang et al., 2019).

6.2.1.5 Soy protein crosslinked with maleic anhydride (SP+MA) bio-adhesive.

The grafting process between soy protein and maleic anhydride takes place by forming amide bonds and reacting with the hydroxyl groups present in the protein (Liu and Li, 2007). Once these bonds are formed, hexamethylenediamine must be added to improve the physicochemical characteristics of the bio-adhesive in terms of strength and water resistance (Liu and Li, 2007). Therefore, the protocol of the bio-adhesive production starts with mixing soy protein with water for 120 min and 60°C before the addition of maleic anhydride, as described by Pizzi et al. (2020). Thereafter, hexamethylenediamine is added after raising temperature to 90°C for a period of 120 min. Finally, with the aim of reducing the water content of the bio-adhesive to 50%, a roto-evaporation is performed at 60°C for 1 h (Xi et al., 2020).

6.2.1.6 Soy protein crosslinked with tannin resin (SP+TR) bio-adhesive.

The production of this type of soy bio-adhesive requires two process steps. The first one is based on the production of the tannin resin, in which the tannin is mixed with methanol, resorcinol, glyoxal and sodium hydroxide at 80 °C for 3 h, thus achieving the formation of a self-crossing structure (Zhou et al., 2013). Second, soy protein, previously mixed with water and stirred for 20 min to obtain a homogeneous suspension, is added to the tannin resin for another 10 min at room temperature (Chen et al., 2017)

The reaction of tannins with soy protein leads to the formation of bonds between polypeptide chains, resulting in an increase in the mechanical properties and moisture resistance of wood boards (Ghahri et al., 2018).

6.2.2 Starch-based bio-adhesives.

Two main starch pre-treatment methods were considered for the analysis: hydrolysis and oxidation.

6.2.2.1 Pre-treatment method 1: Starch hydrolysis

The acid hydrolysis of starch leads to a reduction of its molecular weight, as it is broken down into its monomeric units: amylose and amylopectin. Specifically, amylose is hydrolysed by cleavage of the α-1-4 bond and amylopectin by cleavage of the α-1-4 bond (Chen et al., 2017), using HCl at a temperature below gelatinization (Gu et al., 2010). In this way, a double objective is achieved, on the one hand, the formation of a greater number of active centres for the subsequent polymerization reactions with the crosslinking agents and, on the other hand, a reduction in viscosity, a decisive factor in the mechanical properties required for the application of the bio-adhesive (Cheng and Sun, 2006). After acid hydrolysis, polymerization proceeds, which requires the

development of a grafting process, based on the addition of monomeric units that will be joined by covalent bonds to the amylose and amylopectin units (Haroon et al., 2016). There are different grafting methods, the most widely used are free-radical grafting, as it is the simplest and cheapest way to modify biopolymers (Chen et al., 2015), in which grafting induced by chemical initiators has been chosen for its simplicity and efficiency. The most used initiating agents are sulphate salts (ammonium sulphate, ferrous sulphate), nitrate salts (ceric ammonium nitrate) and also Fenton chemicals (Haroon et al., 2016). After this first stage, the formation of reactive centres in the amylose and amylopectin polymers is achieved, to which the monomers selected for the adhesive formulation, such as polyvinyl alcohol, vinyl acetate or butyl acrylate, will be attached. In this way, a polymerization process takes place, thus improving the mechanical properties of the starch-based bio-adhesive.

6.2.2.1.1 Alternative 1. Hydrolyzed starch bio-adhesive with bio-oil

This alternative considers cassava starch, which has certain advantages over other starch sources, since it has a lower gelatinization temperature, which favours less energy-demanding processes, and also stands out for its structural stability and thermogravimetric properties. After acid hydrolysis at 60°C, the grafting process proceeds, using $(NH_4)_2SO_4$ as the initiating agent. The monomers that bind to the starch structure in the polymerization process are polyvinyl alcohol (PVA), which binds through hydrogen bonds (Tang and Alavi, 2011), vinyl acetate and butyl acrylate, which bind through the free hydroxyl radicals of amylose and amylopectin (Zia-ud-Din et al., 2018).

After this first polymerization, a second one is carried out in the pursuit to improve the thermogravimetric properties of the starch bio-adhesive. For this, it is again required to add an initiating agent, the same as for the first polymerization step (ammonium sulphate). Bio-oil is then slowly added, which will react with the free hydroxyl groups of the amylose and amylopectin units and bind via the formation of ether bonds (Ibrahim et al., 2020). The reason for adding this bio-oil is that its presence in the structure of the bio-adhesive improves its properties: greater stability and resistance to external agents (Xing et al., 2018), such as humidity or temperature variations.

6.2.2.1.2 Alternative 2. Starch bio-adhesive hydrolysed with N-methylol acrylamide

The second starch bio-adhesive alternative is carried out based on three main steps in the formulation procedure: starch pre-treatment based on acidolysis with HCl, followed by linear polymerization, considering the use of three polymers: sodium dodecyl sulphate (SDS), ammonium persulfate (APS) and vinyl acetate (VAc) for 3. 5 h at 70°C, and finally the formation of a network polymer by the addition of N-methylol acrylamide (NMA), requiring 4.5 h and 85°C (Gu et al., 2019). Another aspect to consider is the thermal variability required for each stage of the process. While acidolysis starts at 60°C, it subsequently evolves to reach 90°C. In the case of the linear starch polymerization stage, the process starts at 70ºC and increases to 85ºC in the last 30 min to favour the process yield, and finally a decrease to 50ºC to obtain the final bio-adhesive ready for application for wood panels. As for the type of bond formed between the starch polymer and N-methylol acrylamide, these are strong hydrogen bonds, which favours the improvement of the mechanical properties of the final bio-adhesive, especially in terms of shear and water resistance (Schmidt et al., 2021).

6.2.2.2 Pre-treatment method 2: Oxidation of starch

Pre-treatment by oxidation is also commonly used for structural modification of the native starch molecule. However, it ranks second in terms of preference, since it can lead to partial depolymerization (Fortuna et al., 2002), which is not the case with acid hydrolysis. The result of this pre-treatment is the formation of carboxylic groups or

aldehydes from the oxidation of the primary and secondary hydroxyl groups of the glucose units that make up the amylose and amylopectin polymers (Lewicka et al., 2015). The oxidation of native starch involves the loss of its crystalline form, resulting in the weakening of hydrogen bonds, which will facilitate the bonding of monomeric units in the subsequent polymerization process (Han, 2016).

This oxidative process requires the presence of oxidizing chemicals, such as organic (i.e. NaClO) or inorganic (H_2O_2) peroxides, nitrogen (HNO_2) or metal (CrO_3) compounds, together with a catalyst, which will be transition metals in cationic form (Lewicka et al., 2015). However, the choice of one or the other should focus not only on the performance of the oxidation process, but also on the environmental impacts they may generate. While hydrogen peroxide could be considered as the most "environmentally friendly", the use of metal compounds as oxidizing agents would be the least suitable, from an environmental point of view, as the release of heavy metals into the environment leads to significant environmental impacts (Briffa et al., 2020). After this first oxidative pre-treatment, the polymerization process proceeds, analogously to that presented above for the case of pre-treatment by acid hydrolysis.

6.2.2.2.1 Alternative 3. Starch bio-adhesive oxidized with $FeSO_4$ and H_2O_2

This third alternative is based on the development of a Fenton-type reaction, in which Fe^{2+} is oxidized to Fe^{3+} in the presence of hydrogen peroxide, which is transformed into a hydroxyl radical (Reaction 1). The presence of this radical will result in the oxidation of starch as it reacts with the hydroxyl groups of the glucose units, leading to the creation of carboxylic groups and aldehydes (Kalambur and Rizvi, 2006).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad \text{Reaction 1}$$

After this first pre-treatment step, polymerization is carried out with the following chemicals: PVA, sodium dodecyl sulphate (SDS), ammonium persulfate (APS), silane coupling agent (SCA), butyl acrylate (BAc) and vinyl acetate (VAc) (Zhang et al., 2015) due to a number of reasons: good adhesive strength, better dispersion (Li et al., 2014; Wang et al., 2013), higher adhesion strength, better viscosity (Norström et al., 2018; Wang et al., 2013), water resistance (Gadhave et al., 2019) and thermal stability (Wu et al., 2009).

6.2.2.2.2 Alternative 4. Starch bio-adhesive oxidized with NaClO and ECH.

Unlike alternative 3, in this last starch bio-adhesive option, the oxidative pre-treatment considers the use of NaClO. In this case, the hypochlorite ion (ClO^-) oxidizes the starch molecule by removing the hydrogen atom from the hydroxyl groups and the consequent formation of the carboxylic or ketone groups (Reaction 2).

With this transformation of the molecular structure of starch, an increase in the polarity of the molecule is achieved and a greater facility for the development of the grafting process and subsequent polymerization (Patel et al., 1974).

$$Starch - OH + OCl^- \rightarrow Starch = O + H_2O + Cl^- \qquad \text{Reaction 2}$$

In this study, in addition to including NaClO in this first stage of activation, it also uses epichlorohydrin (ECH) (Nie et al., 2013), which binds to the starch molecule through the formation of diether bridges developing a crosslinking reaction (Kuniak and Marchessault, 1972). PVA, sodium lauryl sulphate (LSS), Tween 80, APS and VAc are also included in the formulation of this bio-adhesive. The advantages of using LSS as an emulsifying compound are based on an improvement in the stability of the adhesive compound, in addition to an increase in shear strength (Din et al., 2020). As for Tween 80, it is a surfactant used to reduce surface tension and improve wetting in the board-adhesive bonding process (Müller and Rath, 2019).

6.3 System boundaries and process inventories definition for LCA

With respect to the system boundaries, all the stages regarding the extraction of raw materials, production of the bio-adhesive and waste management has been considered, thus selecting a "cradle-to-gate" approach for the collection of inventory data (**Figure 24**) corresponds to soy-based bio-adhesives alternatives and **Figure 25** for the starch ones). On the other hand, the transport activities and the infrastructure processes were excluded, as it has been demonstrated that their contribution over the process environmental loads is not significant (Arias et al., 2020; Yang and Rosentrater, 2021).

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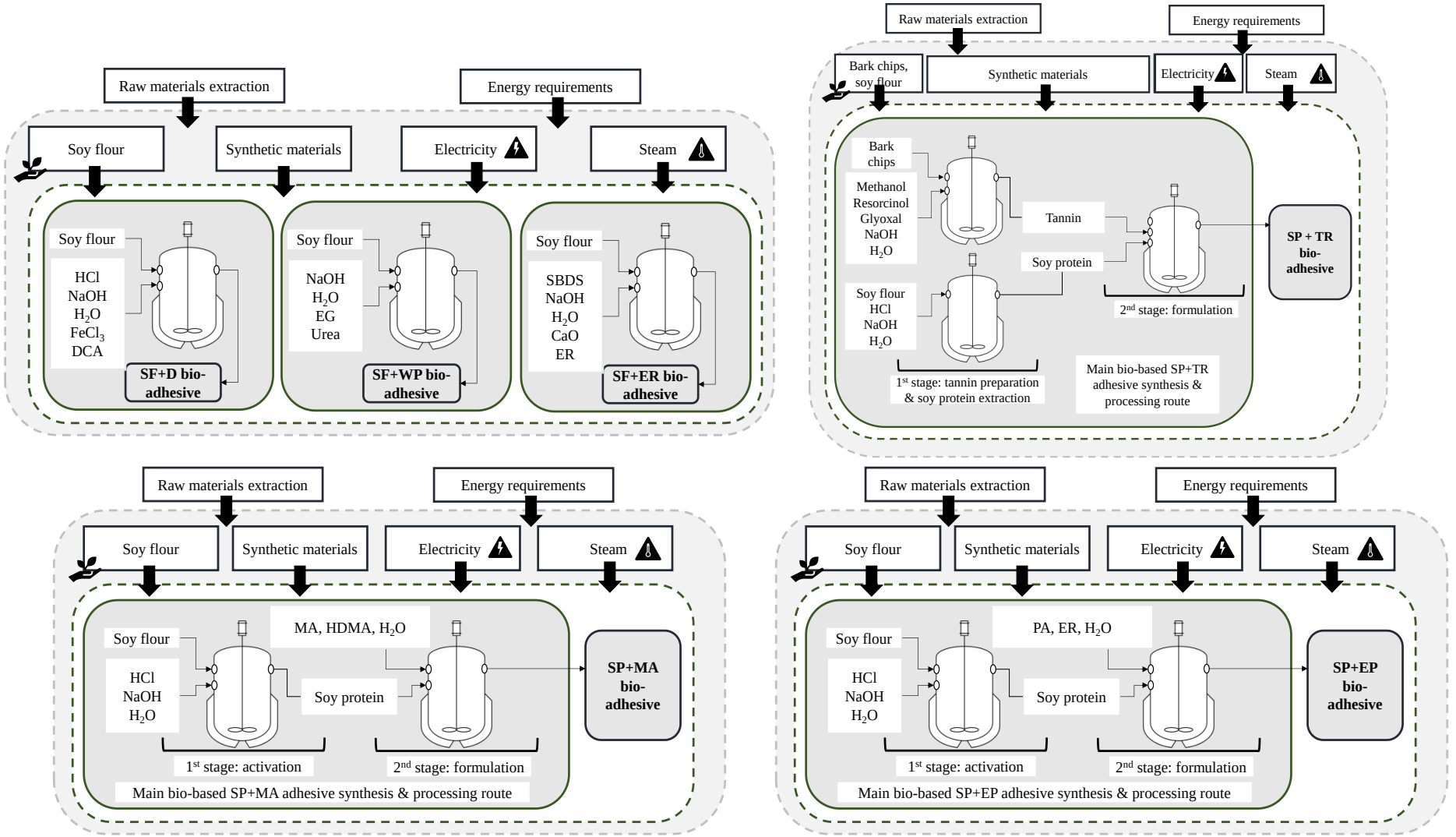

Figure 24. System boundaries considered for the tannin-based bio-adhesives.

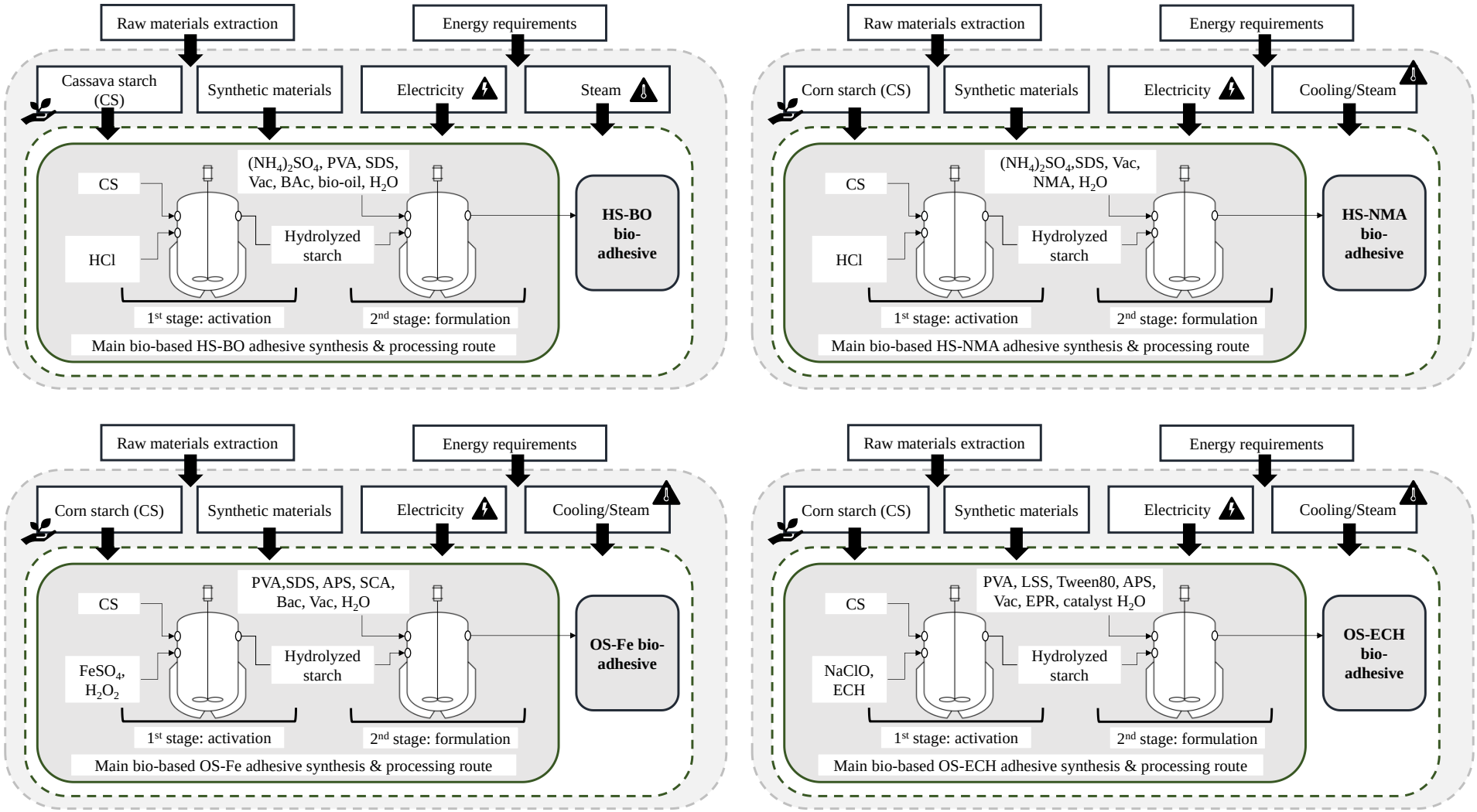

Figure 25. System boundaries considered for the starch-based bio-adhesives.

6.3.1 Definition of the process inventories for LCA

The most significant inventory data for all the aforementioned bio-based adhesive alternatives, considering the production of 1 kg of bio-adhesive as the functional unit are depicted from **Table 13** to **Table 22.**

Table 13. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soybean meal with dicyandiamide crosslinker bio-adhesive (SF+D) production process. Data are reported per functional unit (1 kg of bio-adhesive).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Soybean meal	0.18	kg	SF+D bio-adhesive	1	kg
Tap water	0.78	kg			
Hydrochloric acid	8.31	g			
Ferric chloride	2.25	mg			
Dicyandiamide	7.19	g			
NaOH	20.13	g			
Electricity/heat					
Steam	62.63	kJ			
Electricity	7.15	kWh			

Table 14. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soybean meal enhanced by waterborne polyurethane bio-adhesive (SF+WP) production process. Data are reported per functional unit (1 kg of bio-adhesive).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Soybean meal	0.29	kg	SF+WP bio-adhesive	1	kg
Tap water	0.56	kg			
NaOH	22	g			
Ethylene Glycol	4.40	g			
Urea	4.40	g			
Waterborne Polyurethane	0.12	kg			
Electricity/heat					
Steam	472	kJ			
Electricity	11.53	kWh			

Table 15. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soybean meal crosslinked with SBDS and epoxy resin bio-adhesive (SF+SE) production process. Data are reported per functional unit (1 kg of bio-adhesive).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Soybean meal	0.26	kg	SF+SE bio-adhesive	1	kg
Tap water	0.61	kg			
SBDS	2.61	g			
CaO	6.20	g			
NaOH	12.08	g			
Epoxy resin	0.11	kg			
Electricity/heat					
Steam	1560	kJ			
Electricity	45	kWh			

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Table 16. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soy protein crosslinked with epoxy resin and polyacrylamide bio-adhesive (SP+EP) production process. Data are reported per functional unit (1 kg of bio-adhesive).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Soy protein	0.10	kg	SP+EP bio-adhesive	1	kg
Tap water	0.86	kg			
Polyacrylamide	0.43	g			
Epoxy resin	0.04	kg			
Electricity/heat					
Heat	144	kJ			

Table 17. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soy protein with maleic anhydride bio-adhesive (SP+MA) production process. Data are reported per functional unit (1 kg of bio-adhesive).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Soy protein	0.16	kg	SP+MA bio-adhesive	1	kg
Tap water	0.79	kg			
Maleic Anhydride	0.11	kg			
Hexamethylenediamine	0.21	kg			
Electricity/heat					
Steam	924	kJ	*Emissions to air*		
Electricity	55	kWh	Water vapor	0.27	kg

Table 18. Inputs and outputs of the production process considered for the Life Cycle Inventory for the soy protein with tannin-based resin bio-adhesive (SP+TR) production process. Data are reported per functional unit (1 kg of bio-adhesive). S1 corresponds to the subsystem required for the production of the tannin resin from tannin resource and S2 corresponds to the subsystem of the manufacturing process of the bio-adhesive SF+TR.

INPUTS FROM TECHNOSPHERE (S1)			OUTPUTS TO TECHNOSPHERE (S1)		
Tannin	18.73	g	Tannin resin	48	g
Tap water	14.42	g			
Methanol	4.51	g			
Resorcinol	7.94	g			
Glyoxal	1.05	g			
NaOH	0.96	g			
Electricity/heat					
Heat	44	kJ			
INPUTS FROM TECHNOSPHERE (S2)			**OUTPUTS TO TECHNOSPHERE (S2)**		
Soy protein	0.11	kg	SF+TR bio-adhesive	1	kg
Tannin resin	48	g			
Tap water	0.84	kg			
Electricity/heat					
Steam	241	kJ			
Electricity	12.9	kWh			

Table 19. Inventory data for the production of hydrolyzed starch bio-adhesive with bio-oil (Alternative 1). Detailed data per functional unit (1 kg of bio-adhesive) Acronyms: Polyvinyl alcohol (PVA), Sodium Dodecyl Sulfate (SDS), Vinyl Acetate (VAc), Butyl Acrylate (BAc).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Cassava starch	0.35	kg	Bio-adhesive	1	kg
HCl	0.01	kg			
$(NH_4)_2SO_4$	0.02	kg			
PVA	0.04	kg			
SDS	0.01	kg			
VAc	0.05	kg			
BAc	0.03	kg			
Bio-oil	0.09	kg	*Emissions*		
H_2O	0.44	kg	NH_4Cl	0.014	kg
Electricity/heat			H_2SO_4	0.013	kg
Electricity	0.12	kWh	H_2O	0.017	kg
Heat	58.76	kJ	$(NH_4)_2SO_4$	0.005	kg

Table 20. Inventory data for the production of hydrolyzed starch bio-adhesive with N-methylol acrylamide (NMA) (Alternative 2). Detailed data per functional unit (1 kg of bio-adhesive). Acronyms: Sodium Dodecyl Sulfate (SDS), Vinyl Acetate (VAc), N-methyl acrylamide (NMA).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Corn starch	0.44	kg	Bio-adhesive	1	kg
HCl	16.15	g			
$(NH_4)_2SO_4$	5.09	g			
SDS	5.77	g			
VAc	0.31	kg			
NMA	11.06	g			
H_2O	0.50	kg	*Emissions*		
Electricity/heat			NH_4Cl	6.73	g
Electricity	1.45	kWh	H_2SO_4	0.013	kg
Heat, steam	86.63	kJ	H_2SO_4	32.94	g
Cooling energy	94.52	kJ	$(NH_4)_2SO_4$	0.005	kg

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Table 21. Inventory data for the production of hydrolyzed starch bio-adhesive with N-methylol acrylamide (NMA) (Alternative 2). Detailed data per functional unit (1 kg of bio-adhesive). Acronyms: Sodium Dodecyl Sulfate (SDS), Vinyl Acetate (VAc), N-methyl acrylamide (NMA).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Corn starch	0.06	kg	Bio-adhesive	1	kg
H_2O	0.64	kg			
$FeSO_4$	0.64	g			
H_2O_2	0.64	g			
PVA	0.02	kg			
SDS	0.64	g			
APS	0.64	g			
SCA	0.32	g			
BAc	0.14	kg			
VAc	0.14	kg			
Electricity/heat					
Electricity	0.27	kWh	*Emissions*		
Heat, steam	62.92	kJ	FeH_3	0.23	g
Cooling energy	197.9	kJ	$(NH_4)_2SO_4$	0.005	kg

Table 22. Inventory data for the production of starch bio-adhesive oxidized with NaClO and ECH (Alternative 4). Detailed data per functional unit (1 kg of bio-adhesive). Acronyms: Epichlorohydrin (ECH), Polyvinyl alcohol (PVA), Lauryl Sodium Sulfate (LSS), Ammonium Persulfate (APS), Vinyl Acetate (VAc), Epoxy Resin (ER).

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Corn starch	0.13	kg	Bio-adhesive	1	kg
H_2O	0.41	kg			
NaClO	1.97	g			
ECH	2.63	g			
PVA	0.02	kg			
LSS	2.74	g			
Tween80	4.11	g			
APS	2.81	g			
VAc	0.19	kg			
ER	0.22	kg			
Catalyst	0.01	kg			
Electricity/heat			*Emissions*		
Electricity	0.29	kWh	NaCl	0.83	g
Heat, steam	58.39	kJ	FeH_3	0.23	g
Cooling energy	18.16	kJ	HCl	1.12	g

6.4 Environmental assessment of the alternatives

In the search for the selection of the best alternatives of soy and starch-based bio-adhesives to be used in the manufacture of wood panels, a comparative study is required. First, the ReCipe Midpoint was used to determine the environmental profile of each bio-adhesive based on the impact categories selected for analysis. Although the burdens shown in **Table 23** allow for an overall environmental assessment of the proposed bio-

adhesive alternatives, it is important to conduct a separate study for each to determine the contribution of the components that conform the production system to the overall environmental profile.

Table 23. Characterization results of the starch and soybean bio-based adhesives alternatives considering ReCipe Midpoint as the calculation methodology.

Impact category	Unit	SF+D	SF+WP	SF+SE	SP+EP	SP+MA
GW	kg CO_2 eq	0.61	2.56	1.20	0.71	2.14
SOD	mg CFC_{11} eq	1.62	46.07	2.07	1.08	2.23
TA	g SO_2 eq	1.60	3.41	1.96	1.94	6.39
FE	g P eq	0.19	0.22	0.19	0.30	0.76
ME	g N eq	0.33	0.49	0.43	0.23	1.12
TET	kg 1.4-DCB	0.44	1.00	0.62	0.43	2.19
FET	kg 1.4-DCB	6.14	12.24	10.35	10.42	24.15
MET	kg 1.4-DCB	5.30	12.33	8.46	11.85	31.06
HCT	kg 1.4-DCB	0.01	0.01	0.01	0.02	0.05
HNCT	kg 1.4-DCB	0.04	0.19	0.07	0.48	1.10
FRS	kg oil eq	0.06	0.15	0.30	0.73	0.28
Impact category	**Unit**	**SP+TR**	**HS-BO**	**HS-NMA**	**OS-Fe**	**OS-ECH**
GW	kg CO_2 eq	0.67	0.92	1.67	1.10	1.82
SOD	mg CFC_{11} eq	1.22	2.92	3.24	1.27	1.45
TA	g SO_2 eq	1.95	3.67	8.70	4.06	6.21
FE	g P eq	0.33	0.24	0.85	0.34	0.59
ME	g N eq	0.26	2.17	2.22	0.11	0.26
TET	kg 1.4-DCB	0.40	1.37	2.24	1.05	2.18
FET	kg 1.4-DCB	10.77	0.03	0.08	0.01	1.41
MET	kg 1.4-DCB	12.61	0.01	0.04	0.02	0.06
HCT	kg 1.4-DCB	0.02	0.01	0.01	0.02	0.04
HNCT	kg 1.4-DCB	0.54	0.32	0.14	0.40	0.60
FRS	kg oil eq	0.11	0.28	0.66	0.52	0.81

6.4.1 Environmental profile of the SF+D bio-adhesive

The use of soybean meal is one of the main contributors to the environmental impact associated with the bio-adhesive (**Figure 26**). This contribution is the result of the background processes related with the soybean cultivation processes, specifically on-site emissions from agricultural activities and the use of fertilizers in the cultivation stages. The second main contributor to the environmental profile of this bio-adhesive is the dicyandiamide production process, with a contribution share of more than 50% in half of the impact categories studied. Moreover, this chemical compound has some potential to cause toxicity to aquatic species. Although it is a stable compound under normal conditions, its decomposition results in the release of carbon monoxide, carbon dioxide and nitrogen oxides, recognized as GHG emissions. Due to these potential effects on the environment, the possibility of substituting it with another crosslinking agent should be studied, or considering that this process is not optimized, a reduction in the dosage used for the formulation of the bio-adhesive could be proposed.

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Another relevant aspect in the selection of a cross-linking agent. Beyond its contribution to the environmental profile, its potential adverse effect on human health must also be considered. When developing a new product, it is important not only to study the environmental impact of the process, but also whether the use of the product could pose a risk to human health and natural ecosystems in terms of toxicity. According to the EU classification, dicyandiamide is a compound that, although it does not have carcinogenic or mutagenic effects, as was the case with formaldehyde, its exposure could lead to certain potential health effects, such as skin irritation, methemoglobin formation if absorbed into the body and gastrointestinal discomfort if inhaled. Although the concentration of dicyandiamide used for the formulation of the proposed bio-adhesive is low, which considerably reduces its potential adverse effects, the potential for toxicity must be assessed in the weighting for the selection of different bio-based alternatives.

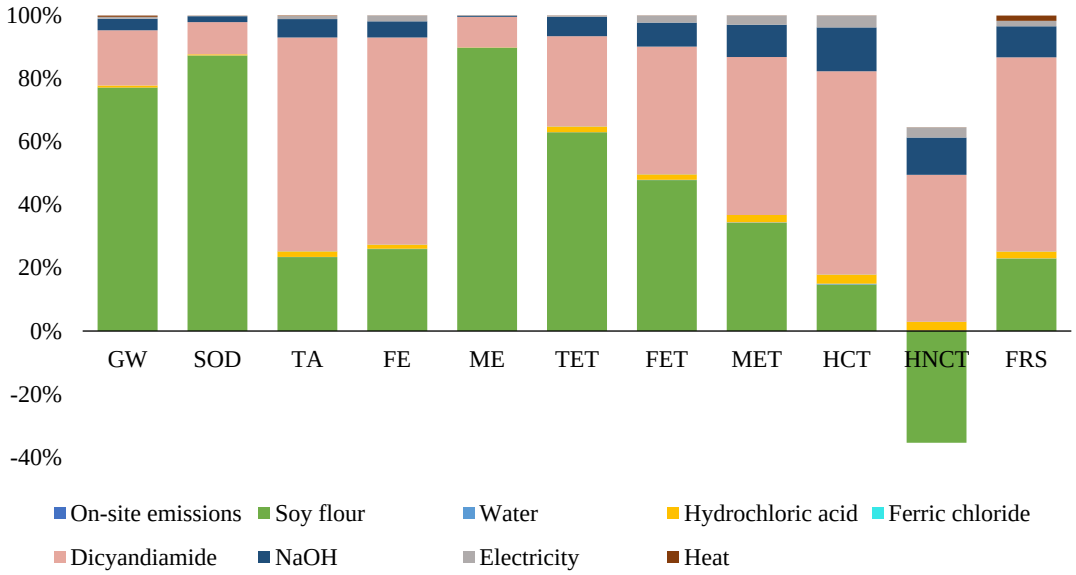

Figure 26. Environmental profile of SF+D bio-adhesive

6.4.2 Environmental profile of the SF+WP bio-adhesive

Two main hotspots could be identified in this environmental profile (**Figure 27**): soybean meal and waterborne polyurethane as the cross-linking agent. This compound is obtained from non-renewable sources, specifically, it is produced by a petrochemical route (Yu et al., 2014)**,** which leads to the emission of pollutants to air, water and soil.

As an alternative to improve the environmental profile of this bio-adhesive, different recent works have been developed on the production of adipic acid, one of the compounds used for the formulation of WPU, through a biological synthesis (Kruyer et al., 2020; Raj et al., 2018; Sun et al., 2018), thus avoiding the use of the petrochemical route.

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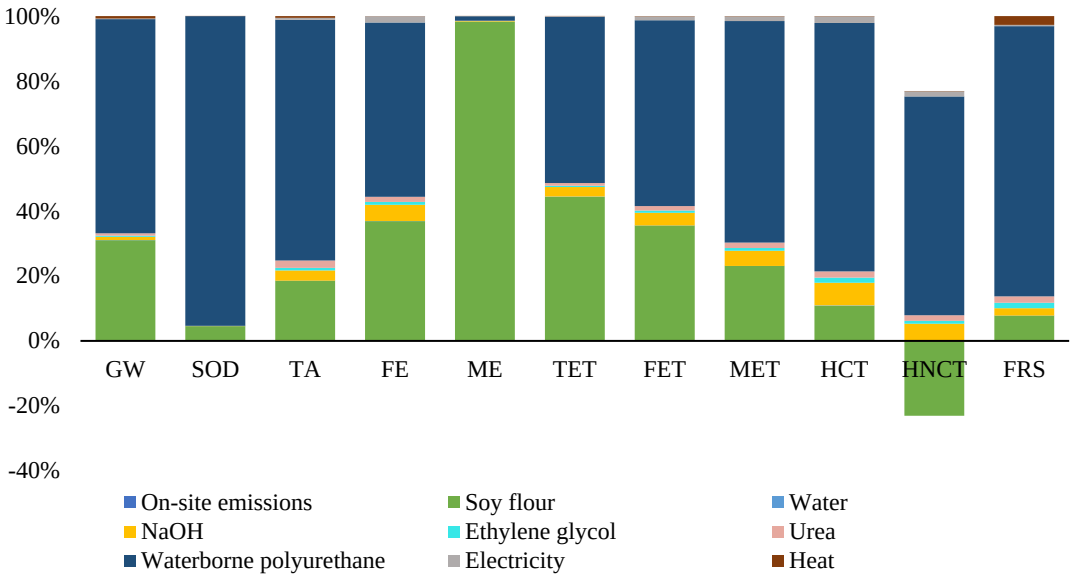

Figure 27. Environmental profile of SF+WP bio-adhesive

6.4.3 Environmental profile of the SF+SE bio-adhesive

The environmental impact results (**Figure 28**) showed that the background activities related to the production of soybean meal and epoxy resin play a key role in the environmental profile in all the MidPoint categories considered for the assessment. In terms of the contribution derived from chemical use, the only one that stands out is in the fossil resource scarcity category, derived from epoxy resin production. There is also some involvement in the categories of ecotoxicity, eutrophication and acidification. Its release into the aquatic environment causes reproductive effects on aquatic organisms, and in terms of toxicity to soil and plants, epoxy resin could be rapidly taken up by roots and metabolized into glycosidic compounds (Carlisle et al. 2009), causing potential harmful effects on seeds, leaves, stems, etc. (Plumlee, K. 2004).

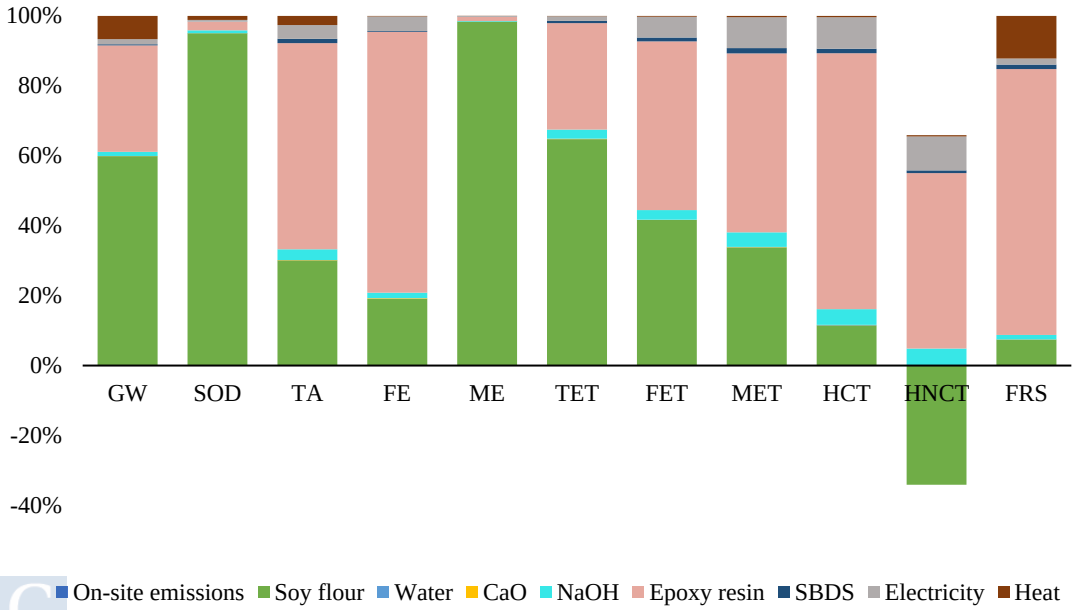

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Figure 28. Environmental profile of SF+SE bio-adhesive

6.4.4 Environmental profile of the SP+EP bio-adhesive

Bearing in mind the results depicted in **Figure 29**, the environmental profile is dominated by the impacts derived from the background processes of soybean meal production. Therefore, the main cause of the contribution of soy protein is the result of the combination of energy consumption associated with the extraction process and the background processes required in agricultural cultivation. The reason for the environmental contribution of the epoxy resin is analogous to that mentioned in the previous environmental profile assessment.

Although the contribution of polyacrylamide is not significant in the environmental profile of this bio-adhesive, its hazard classification should be taken into account. According to EU classification labels, exposure to this substance may have a number of adverse effects due to its potential for carcinogenesis and mutagenesis, acute toxicity if ingested, inhaled or in contact with eyes, and it is also suspected to contribute to impairment of fertility. Due to the classification of this substance, although its content in the bio-adhesive formulation is relatively low, which reduces its potential risk to human health, it is an aspect that should be anticipated, as it may be a cause for exclusion in the selection of the best bio-adhesive alternative.

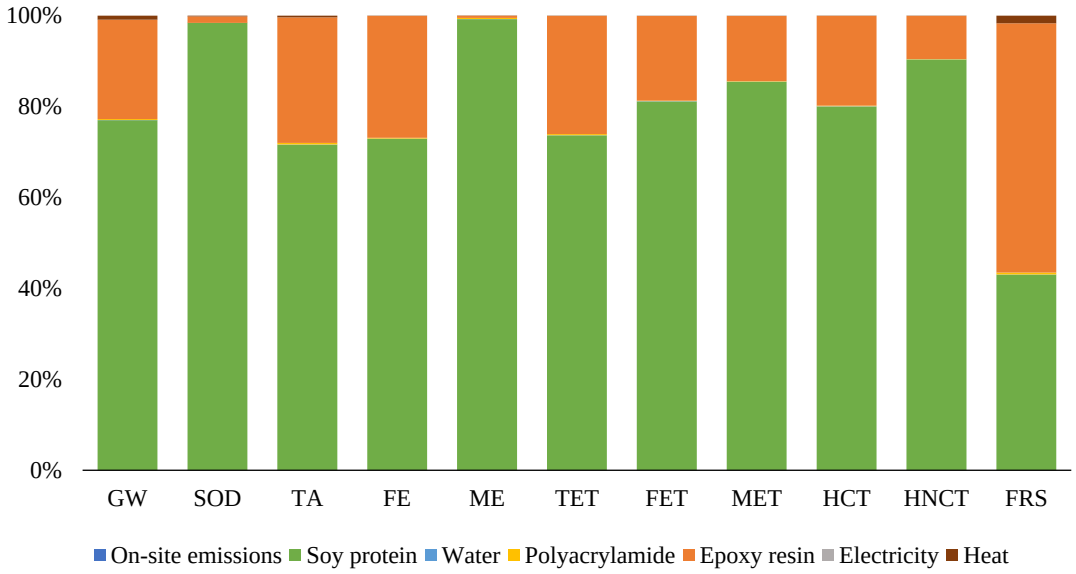

Figure 29. Environmental profile of the SP+EP bio-adhesive

6.4.5 Environmental profile of the SP+MA bio-adhesive

The distribution of burdens shown in **Figure 30** shows that HDMA production is the main hotspot in the global system profile, with a share of more than 40% in categories such as GW, TA, ME, TET and FRS. The reason for the environmental contribution of maleic anhydride is the result of the energy needs of its production based on fossil resources. Again, as in the previous environmental profiles, the contribution of soybean is also significant, mainly related to the extraction of soy protein.

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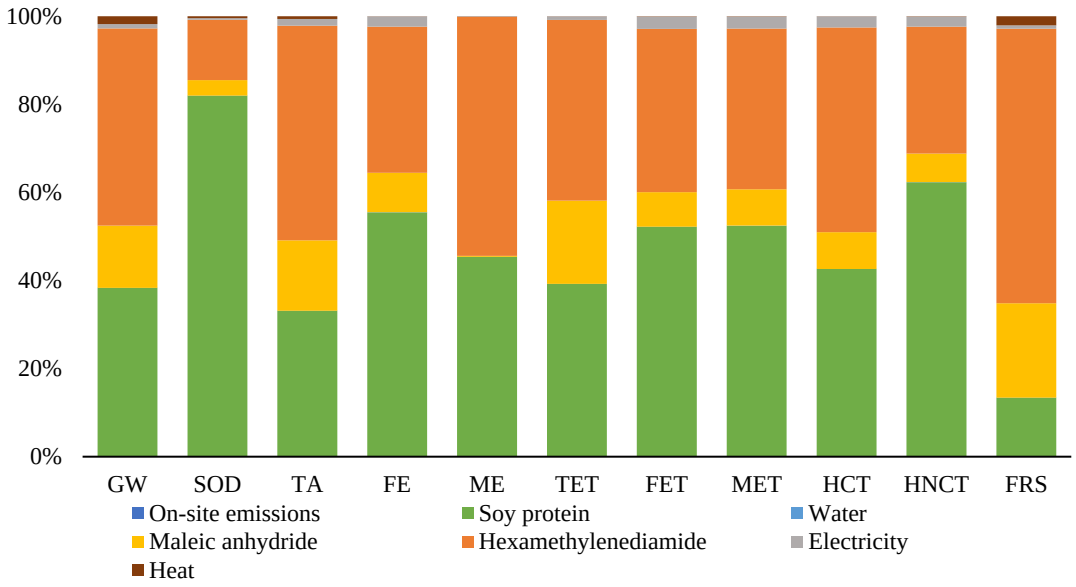

Figure 30. Environmental profile of the SP+MA bio-adhesive

6.4.6 Environmental profile of the SP+TR bio-adhesive

The results obtained for the environmental profile of the adhesive showed that the use of tannin-based resin is a good choice as a crosslinking agent, since its environmental contribution on the whole system is not very significant **(Figure 31**). As for the above scenarios, the contribution of soy protein extraction is remarkable. Therefore, optimizing the protein extraction process, or even reducing the amount of soy protein used for formulation, is a key aspect to improve the environmental profile and yield of this bio-adhesive option.

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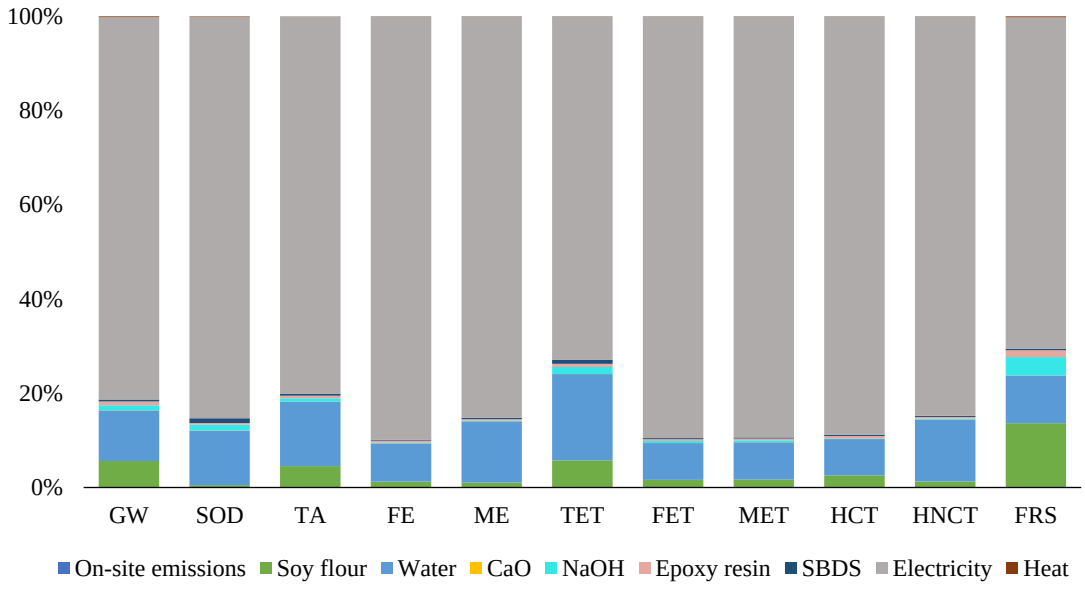
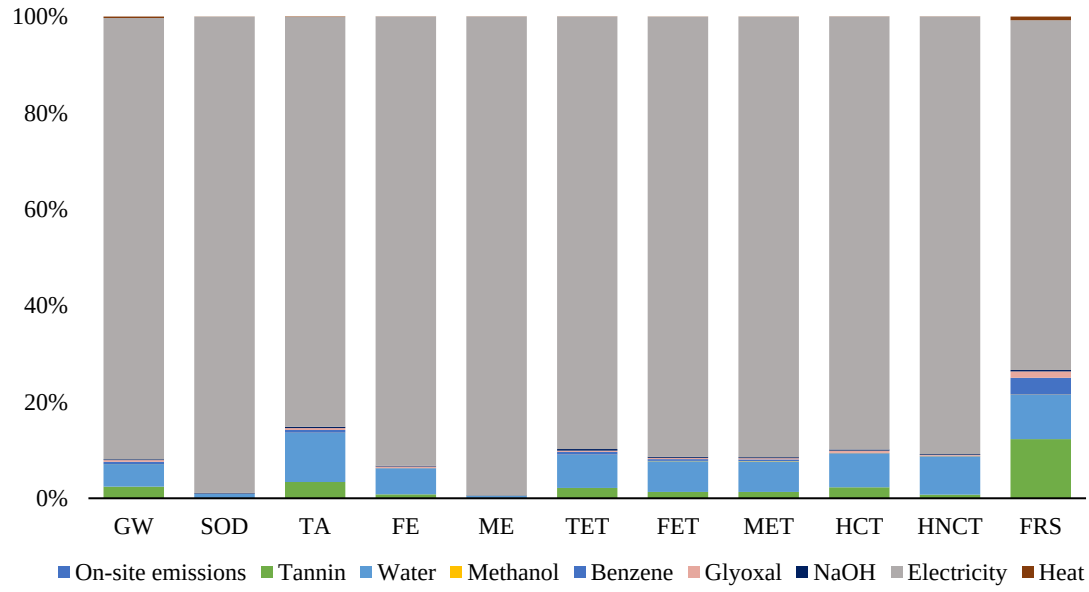


(a)



(b)

Figure 31. Environmental profile of SP+TR bio-adhesive considering (a) the formulation of the adhesive and (b) the production of the tannin resin.

6.4.7 Environmental profile of the HS+BO bio-adhesive

There is some variability in the environmental contribution according to the impact categories, although three main hotspots can be identified: cassava starch production, electricity requirements and emissions from the bio-adhesive formulation (**Figure 32**). The reason for the significant environmental contribution of starch is attributed to cassava cultivation due to the direct emissions of CO_2, ammonia and nitrates as a consequence of the use of fertilizers in the crop field and the generation of crop residues, and the use of diesel fuel for agricultural machinery.

Emissions are characterized by ammonium compounds, specifically ammonium chloride and ammonium sulphate, as well as sulfuric acid. While ammonium species cause eutrophication (USDA and NOP, 2018), the implication of sulfuric acid can cause variations in the pH of the aquatic environment, with a moderate toxicity potential (Daryl Quinlivan, 2020).

In the FE category, the impact of the electricity needs of the production process of this bio-adhesive alternative stands out. The reason for its contribution in the impact category is associated with the production of electricity from non-renewable fossil resources. It should also be noted that energy consumption involves the formation of atmospheric ozone as a product of the reaction between nitrogen oxides and volatile organic compounds, when exposed to sunlight (Babaee et al., 2020).

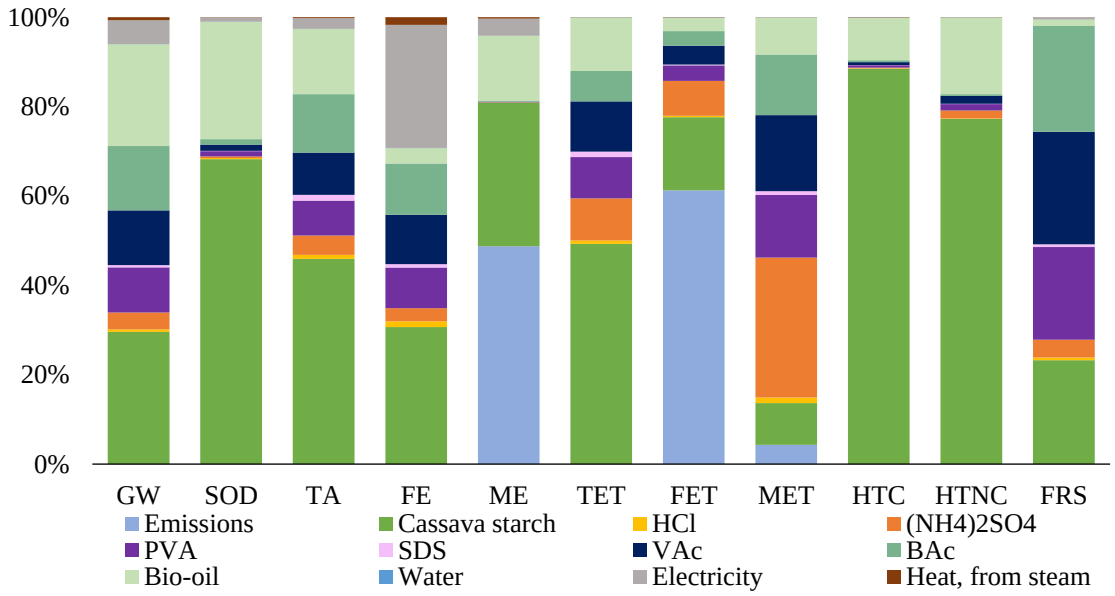


Figure 32. Environmental profile of the hydrolyzed starch bio-adhesive with bio-oil (HS-BO)

6.4.8 Environmental profile of the HS+NMA bio-adhesive

A analogy can be observed in the environmental profile of this option compared to the results shown above in **Figure 33**. Although there is a greater environmental influence from electricity consumption. If the inventory of this process is analyzed, it is observed that the electricity needs per kg of bio-adhesive produced is 10 times higher (the processing time is also longer, being in this case 12 h of batch process, compared to 7 h of the first alternative studied). This is the reason why the contribution of electricity in the environmental profile is more remarkable for this second bio-adhesive option. A promising and sustainable way to improve this environmental profile would be to consider the use of renewable energies, which would not only avoid the depletion of fossil resources but would also reduce the emissions associated with the raw material extraction processes and the production process itself.

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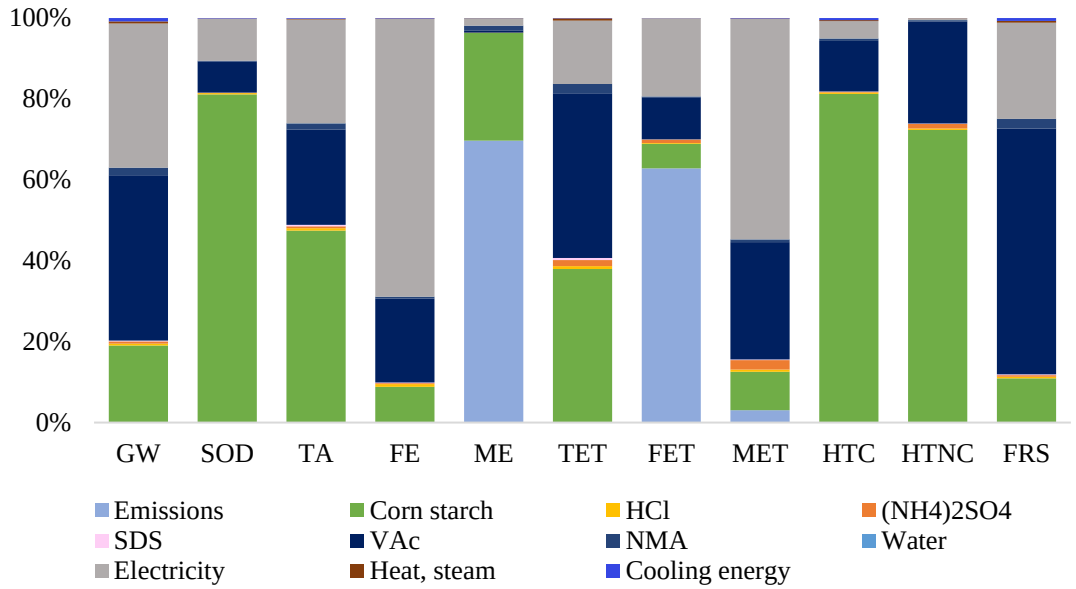

Figure 33. Environmental profile of the hydrolyzed starch bio-adhesive with bio-oil (HS-NMA)

6.4.9 Environmental profile of the OS+Fe bio-adhesive

Both butyl acrylate (BAc) and vinyl acetate (VAc) account for more than 50% of the environmental contribution in most of the impact categories of this third alternative (**Figure 34**), except for the SOD, ME and HT categories, where a higher impact influence of corn starch is perceived.

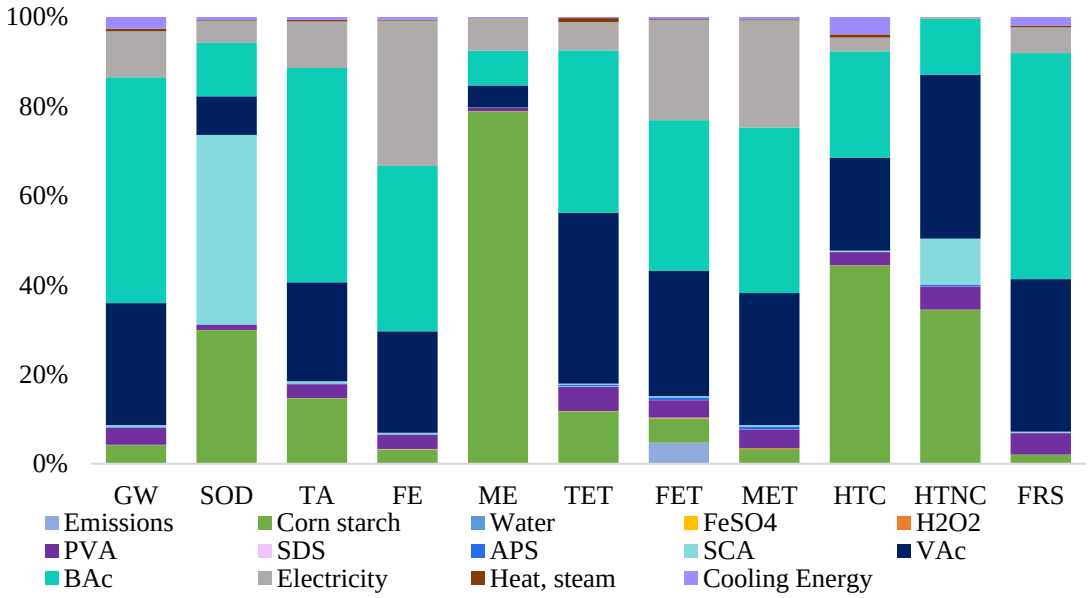

Figure 34. Environmental profile of the oxidized starch bio-adhesive with iron sulfate and peroxide (OS-Fe)

The background manufacturing activities of BAc and VAc are the reason for these high contributions in the environmental profile for this third bio-adhesive alternative. As for BAc, it is produced by the esterification reaction of acrylic acid with methanol. Developing the LCA of its production, it is observed that methanol and the caloric requirements of the production process are the main hot spots in the environmental

profile. On the other hand, when performing an in-depth analysis of the methanol manufacturing process, which is based on the hydroformylation of propylene, the main contributors to its environmental profile are carbon monoxide, propylene and energy requirements. Therefore, this detailed analysis of BAc background activities allows us to identify that its contribution to the environmental profile of the starch bio-adhesive is the result of the use of chemicals (methanol, carbon monoxide and propylene), which are the cause of the high contribution in categories such as GW, OF, TA, TET, FET and MET. On the other hand, thermal energy needs, obtained from non-renewable fossil resources, are the source of the impact in the MRS and FRS categories.

A similar procedure has been carried out to investigate the high contribution of VAc in the environmental profile obtained. The conclusion obtained after an exhaustive analysis of each of the stages of its production process, based on the reaction between ethylene and acetic acid, is that the chemicals with the greatest impact on the environment are acetic acid, carbon monoxide and methanol (mainly affecting the impact categories of ecotoxicity, eutrophication and climate change) and, on the other hand, energy requirements, which contribute to the categories of scarcity of resources, both fossil and mineral.

6.4.10 Environmental profile of the OS+ECH bio-adhesive

Figure 35 represents the environmental profile of the starch bio-adhesive oxidized with NaClO and ECH. As can be seen, two main items stand out in most of the impact categories: epoxy resin and corn starch, except for FET, MET and MRS. Regarding the FET and MET categories, the on-site emissions of the bio-adhesive production process are the ones with the highest environmental contribution. The use of NaCl, HCl and H_2SO_4 is the reason for the high impact obtained in the categories of freshwater and marine ecosystem ecotoxicities. An appropriate neutralization strategy would allow reducing the environmental contribution in these impact categories. As for corn starch, its influence on the environmental profile is the result of background activities, as analyzed in the previous profiles obtained for the other bio-adhesive alternatives proposed here: use of fertilizers in cultivation, use of energy for machinery, among others.

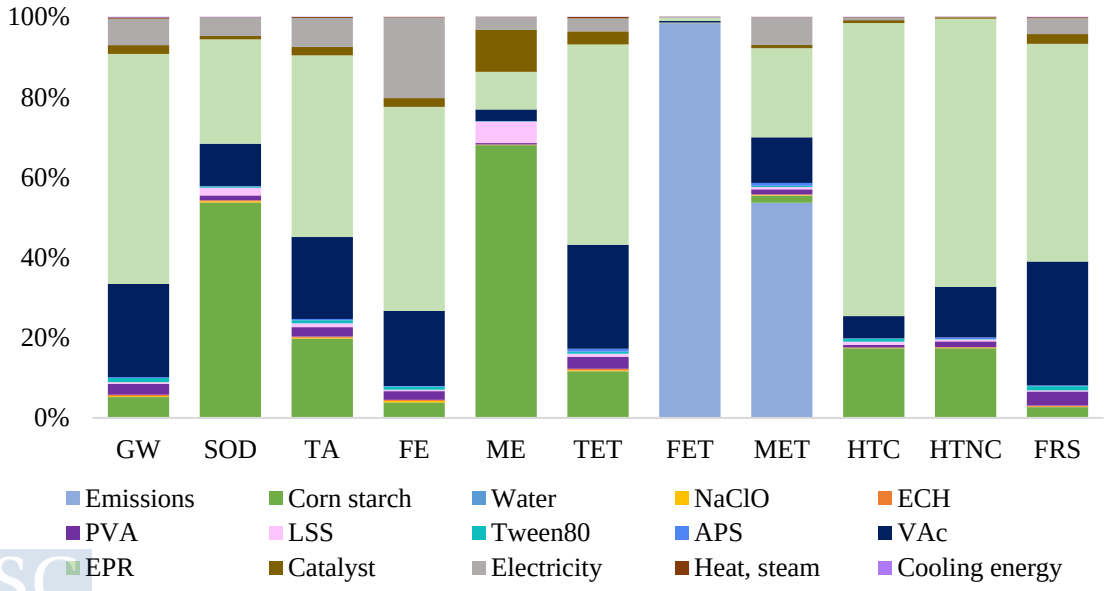

Figure 35. Environmental profile of the oxidized starch bio-adhesive with ECH (OS-ECH)

Looking for the reason for such a high environmental contribution of the use of epoxy resin, the elements that make up its production process have been analyzed to determine if this high impact is a consequence of the use of chemicals or if, on the contrary, it is due to the energy demand of its industrial production. Epoxy resin is produced from the reaction between Bisphenol A and epichlorohydrin, both chemicals are obtained from non-renewable fossil resources and are the main hotspots identified in the environmental profile. As for Bisphenol A, it is produced by catalytic condensation between phenol and acetone. To evaluate the reason for its high impact, a detailed analysis of its manufacturing process is performed, based on the Hock process (Rhee et al., 2006), an autocatalytic and exothermic oxidation process using cumene as raw material, identifying cumene as the main hot spot in the environmental profile obtained. Thus, a final analysis was carried out for this chemical, obtained from the alkylation of benzene and propene and, once again, it was observed that the elements of the inventory that entail the greatest environmental impact are the chemicals used for its production, given its non-renewable nature. As for epichlorohydrin, the conclusions obtained by performing an analysis similar to the previous one are the same, although, in addition to the identification of chemicals as the main contributors to the environmental impacts generated, the emissions associated with the production processes also have a significant influence, given that its most widespread form of waste management is by incineration, which gives rise to emissions of hazardous agents, such as carbon dioxide, methane, nitrates and phenolic compounds, among others.

Therefore, after this exhaustive analysis, it is concluded that the chemicals necessary for the formulation of this starch bio-adhesive alternative are the main causes of environmental impacts.

6.5 Sensitivity analysis and alternative formulation of the bio-adhesives

The previous sections have shown that some components of the inventories make a greater contribution to the environmental loads of the alternative bio-adhesives evaluated. In this sense, with the aim of providing improved scenarios, with reduced environmental loads, this section develops sensitivity analyses, seeking to identify how the profiles could be improved and which are the main aspects to work on.

6.5.1 Soy based bio-adhesives.

Although the results obtained for soybean bio-adhesives are promising, their environmental profiles could be even better if the main critical points previously identified for each bio-adhesive were improved and optimized. In the case of the adhesives that required the protein extraction stage, it was observed that the energy requirements of the process contributed significantly to the environmental profile, so that, by developing an energy optimization of the production process, they could be reduced by up to 25%. On the other hand, it has also been found that the use of certain chemical products as crosslinking agents has an important contribution to the environmental profile obtained, as has been reported in the case of the use of dicyandiamide, WPU, epoxy resin and, above all, hexamethylenediamine. Therefore, a sensitivity analysis has been developed focusing on the reduction of the amount of chemical dosage, assuming that the reduction of the amount of cross-linking chemical by 20% in the bio-adhesive formulation. The first case considered for study (**Figure 36A**) refers to the reduction of the amount of dicyandiamide used for the formulation of the SF+D bio-adhesive. The greatest environmental improvement is observed in the categories of TA, FE and FRS, where impact reductions of 13%, 14% and 12%, respectively, has been obtained. It should

be noted that in the GW, SOD and ME categories no significant changes are observed compared to the base case. The reason for this low level of improvement is due to the fact that the main contributor in these impact categories is not the use of dicyandiamide, but the background activities associated with soybean production.

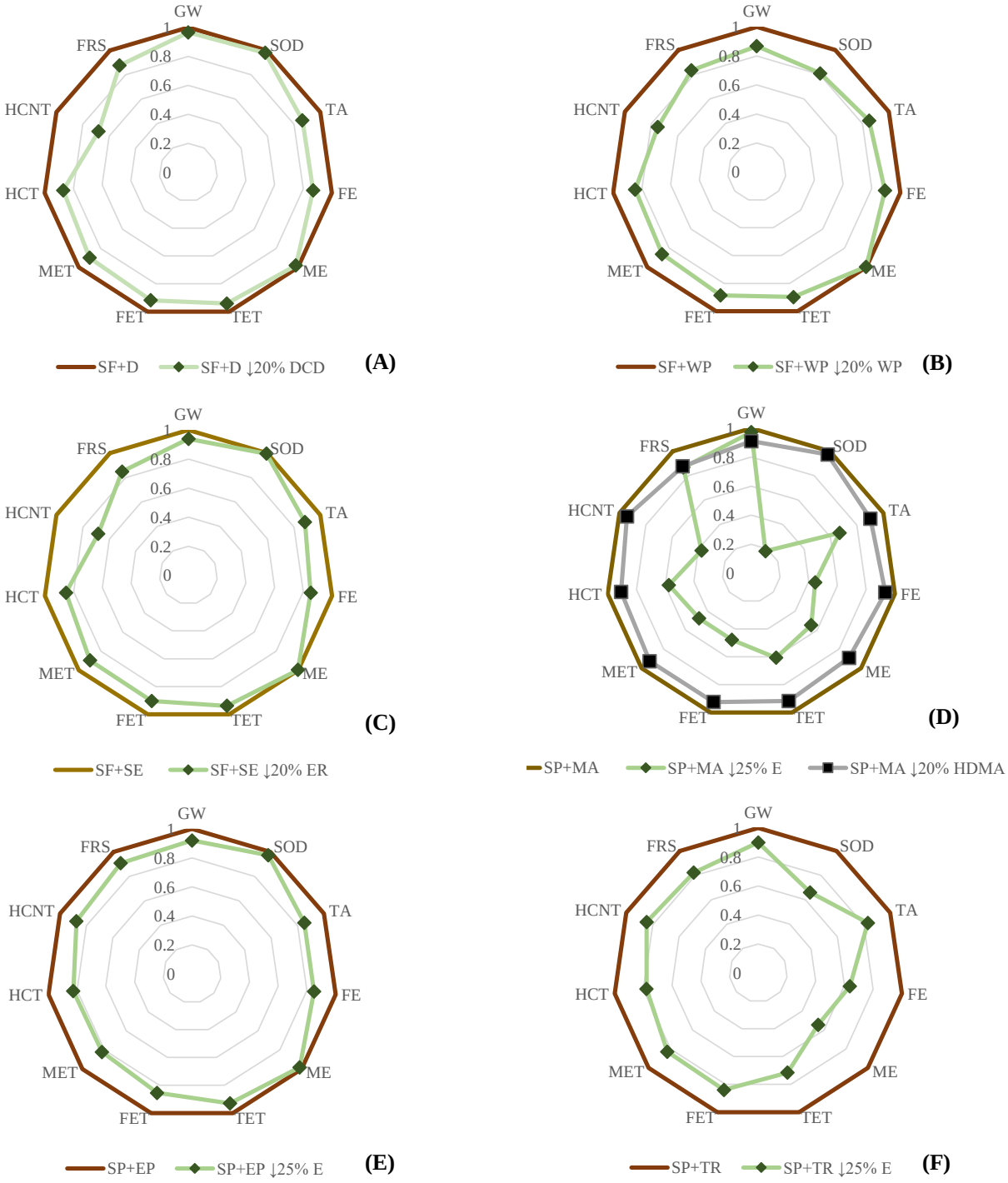

Figure 36. Sensitivity analysis of bio-adhesives production processes under study; (A) Reduction of 20% on dicyandiamide dose on SF+D (B) Reduction of 20% on WPU dose on SF+WP (C) Reduction of 20% on epoxy resin dose on SF+SE (D) Reduction of 20% on HDMA dose on SP+MA and 25% of electricity needs for protein extraction (E) Reduction of 25% on electricity needs on soy protein extraction process for SP+EF and for (F) SP+TR bio-adhesives.

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The second bio-adhesive alternative is the SF + WP, in which it was proposed to reduce the dose of WPU used for the adhesive formulation. The results obtained showed a significant improvement in the environmental profile, reaching reduction percentages of up to 20% (**Figure 36B**). The only impact category in which the improvement obtained is negligible in the ME. As in the previous analysis, the environmental contribution in this impact category is the result of soil management and agricultural activities associated with soybean cultivation.

In the case of the reduction in the dose of HDMA used for the production of the SP + MA bio-adhesive, improvement percentages of between 13% and 14% have been achieved for the impact categories of ME, TET and FRS (**Figure 36C**). The formulation of this adhesive requires the soy protein extraction process, a step that requires significant energy consumption, resulting in a high contribution to the environmental profile obtained for the adhesive. The fact that two critical points of the bio-adhesive production process are identified means that, although an improvement in the environmental profile has been obtained by reducing the dose of crosslinker used, the impact reduction values are not as high as desired. A joint reduction of the two main contributors to the system would lead to a more significant improvement in the profile.

The last alternative focused on reducing the amount of crosslinking agent used for the formulation is the SF+SE bio-adhesive (**Figure 36D**). The use of epoxy resin for the bio-adhesive formulation involves the use of non-renewable fossil resources. Therefore, a reduction in the dosage of this chemical used leads to a significant improvement in the SF+SE impact category, reaching a percentage reduction of 15%. However, in the SOD and ME categories, the impact reduction percentages are less than 1%. The reason for this low value is that in these categories the soybean protein extraction process, together with the background activities associated with its cultivation, are the main contributors.

The most significant improvements in the environmental profiles have been achieved by reducing the electrical requirements of the soy protein extraction process by 25% (**Figure 36E**). The highest percentages of improvement were obtained in the FE (22%), MET (21%) and FRS (20%) categories. The only impact categories where the improvement was not as high as expected were SOD and ME, where the percentages of impact reduction were 3% and 2%, respectively. In these categories, the influence of the background activities of soybean cultivation is very significant, reaching practically the entire impact generated.

6.5.2 Starch based bio-adhesives.

A certain analogy has been observed among the main contributors to the environmental impact in the four starch-based bio-adhesives evaluated, with the raw material itself, starch, being one of the main hot spots in the environmental profile, given the background activities necessary. A more sustainable practice in the agricultural stage would imply a significant reduction of the impact, such as less use of fertilizers, control of water flows, efficient irrigation practices and harvesting systems with efficient machinery. Therefore, it is expected that, based on these modifications, the impact of starch could be reduced by 20%.

In addition to starch, another element that represents certain impact are the emissions associated with the production process, both in the pretreatment stage to obtain hydrolyzed or oxidized starch, and in the adhesive formulation stage. The installation of emission capture systems, as well as a more effective control of the outputs of the facility, would mean a reduction of the outputs with environmental impact. Through this practice, a 20% reduction in process emissions could be expected.

In terms of energy consumption, the profile in which electricity makes the greatest contribution is that of the hydrolyzed starch bio-adhesive cross-linked with NMA (HS-NMA). In order to reduce it, it has been decided to (1) improve the energy efficiency of the process through a detailed analysis of the process and the identification of the equipment with the highest electricity demand and (2) opt for the use of renewable energies to obtain electricity instead of using fossil fuels. Taking into account these two modifications, it is expected to be able to reduce electricity, for case (1) by 20%, while for case (2) it has been chosen to consider a mixed electricity with several renewable sources of electricity generation (tidal, wind, hydro, etc.).

Finally, other major hotspots identified are chemical compounds, mainly PVA, VAc, BAc and EPR. Their production processes involve the use of fossil-based energy, other chemicals that can have a high impact, as well as a number of associated emissions that translate into a significant impact on the environmental profiles of bio-adhesives. Given this it has been chosen to reduce their usage rate by 20%, which could be achieved by improving productivity and process yield. In addition, future research should focus on alternative options for these crosslinking agents in order to promote more sustainable bio-based adhesives. Each of these considerations, as well as variations in impact from the base cases previously studied, can be seen in **Figure 37**.

For the case of the HS-BO alternative, it can be seen that the decrease in the use of starch for bio-adhesive formulation is the sensitivity scenario that provides the best environmental results, with the SOD, HTC and HTNC impact categories showing the highest reduction values, with more than 20%. The only impact category where no reduction is observed is for MET, since the contribution of starch on the environmental profile of the bio-adhesive base case is not so significant. When evaluating the alternative of reducing the emissions related to the formulation process, some improvement is observed in the impact categories FET and ME, more or less around 10%, while when thinking about the decrease in the dose of PVA used, only in the case of FRS some variation is observed, which means a decrease in the environmental load of around 5%. In this sense, it can be concluded that increasing the productivity and yield of the formulation to reduce the amount of starch required per kg of bio-adhesive is the best alternative to decrease the environmental loads.

A similar result is obtained when performing the alternative scenarios for the OS-Fe scenario, since the reduction on the dose of starch required per kg of formulated bio-adhesive is the best option in the way of reducing environmental loads, reaching reduction values of 15% for the ME category and 9% for the HTC category. On the other hand, it is worth mentioning that for certain impact categories no reduction is observed, as is the case for GW, FE, MET and FRS. For these mentioned impact categories, the reduction values are achieved by reducing the amount of chemicals used for adhesive formulation, in particular with the reduction of VAc and BAc doses in a 20% value. The reduction values obtained are similar for mostly all the impact categories, with the exception of HTNC, FRS and GW, in which, for the HNTC, the reduction on the dose of VAc provides higher percentage of reduction (about 7%), while only a 2% for the BAc. In the case of FRS and GW, is the dose of Bac the one that improves more significantly the environmental loads obtained, achieving reduction values of 10% for each of them.

When evaluating the alternative scenarios for the HS-NMA bio-adhesive, a new proposal is provided in comparison with the last two alternatives evaluated, since for this bio-adhesive the contribution of the electricity requirements is notorious on some impact categories of the environmental profile of the base case. In this sense, for most of the evaluated categories, the reduction of electricity requirements and the use of renewable resources for the production of this energy, are the sensitivity scenarios that provide the

best results, reaching reduction values that amount to 60-80% for the impact categories ME, FET and GW, when renewable electricity is used. In this case, the reduction obtained by the reduction in the chemical dose of VAc is not so significant, reaching the highest reduced value for the FRS impact category, but less than 10%. On the other hand, as for the previous scenarios, the use of starch implies a significant burden on some categories, and for this case, its reduction on the bio-adhesive composition by 20% implies environmental improvements on the impact categories HTNC, HTC, SOD and ME, with values between 10-20%, approximately. Comparing all the reduced results obtained, it could be concluded that advocating the use of renewable electricity is the best option from an environmental point of view.

Lastly, for the OS-ECH bio-adhesive alternative, some differences could be evidenced in comparison with the sensitivity scores obtained by the before discussed scenarios. In this case, the reduction on the crosslinker dose, the epoxy resin (EPR), really implies a reduction on the environmental loads in every impact category under evaluation, with the exception of ME and FET. The reduction values are encountered between 5-15%, being the highest reduction value the one achieved for HTC impact category. On the other hand, it is worth mentioning that the highest reduction is achieved for the FET category, reducing emissions by 20%, and a 10% reduction is also observed for the MET category. It is considered that this reduction in emissions could be achieved through the application of appropriate technology and equipment for emissions capture. Finally, as in the previous scenarios, advocating for the reduction of the amount of starch required for the formulation of the final bio-adhesive also implies significant improvements in environmental loads, mainly observed in the SOD, ME, FET and MET impact categories.

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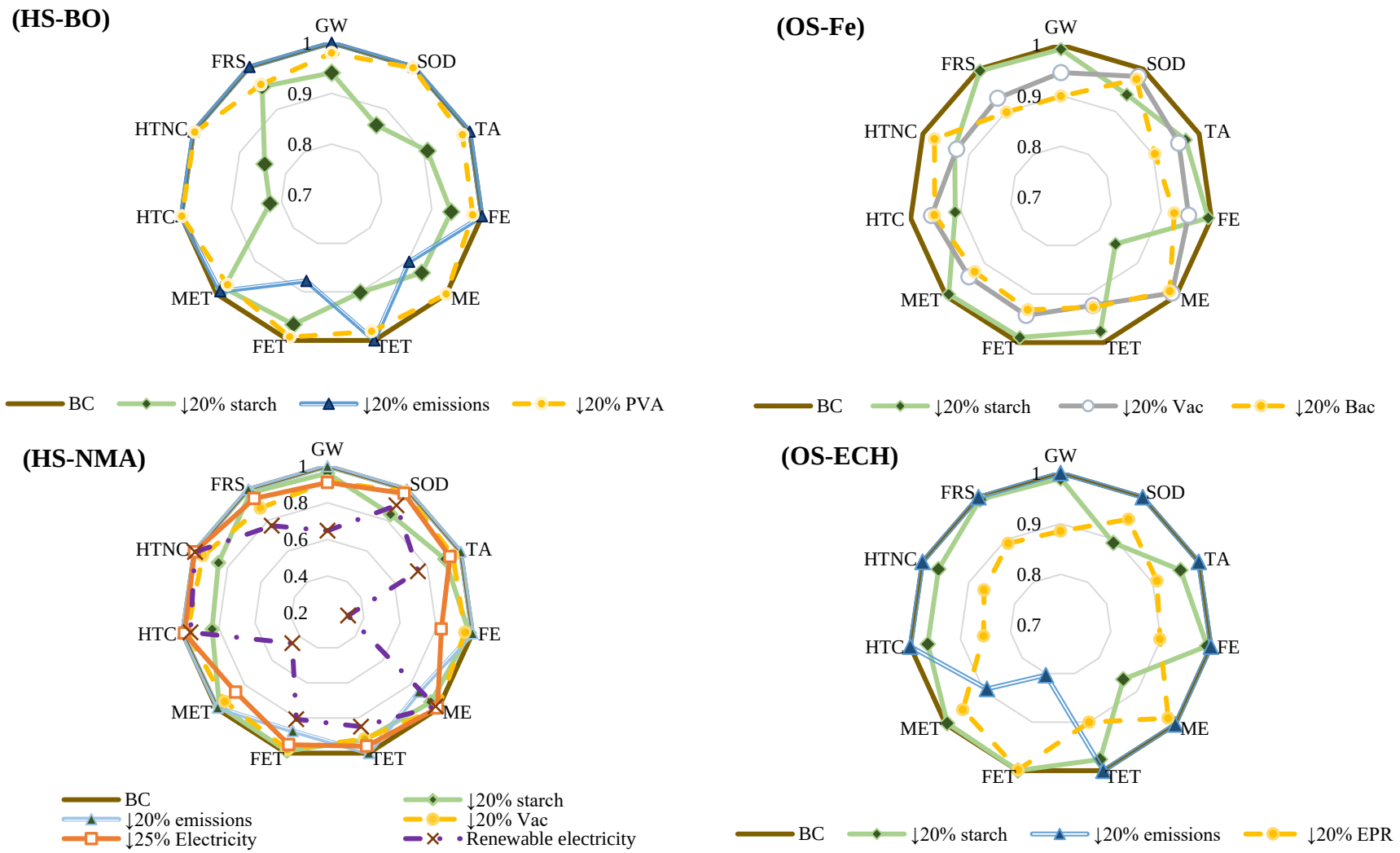

Figure 37. Sensitivity analysis of starch bio-adhesives production processes under assessment

6.6 Comparison between base case scenarios

In order to identify the best scenario for the production of wood bioadhesives, a comparative evaluation has been carried out, firstly, among the scenarios by raw material, secondly, among all the evaluated scenarios of bio-based nature and, finally, with the most commonly used synthetic resins, and based on formaldehyde, which are UF, PF and MUF.

6.6.1 Soy based bio-adhesives.

As it could be seen in **Figure 38**, the soy bio-based adhesive that implies the higher environmental loads is the soy protein crosslinked with maleic anhydride (SP+MA) for all the impact categories with the exception of GW and SOD, for which the alternative soybean meal cross-linked with waterborne polyurethane (SF+WP) has the highest impact. It is also this alternative that has the highest impact when compared to the other scenarios for most of the remaining impact categories, with only three exceptions: FE, HCT and FRS, in which the environmental loads obtained for SP+TR, SP+ER and SF+SR imply a higher value of impact.

In order to provide a better analysis for the scenarios other than SP+MA and SF+WP, that clearly are the ones with the highest impact, **Figure 38** (**bottom figure**) is presented, without considering those scenarios, just to have a better understanding of the effects of the remaining scenarios on the environmental loads. As can be seen, the bio-based adhesive with the lowest environmental impact is the soybean meal crosslinked with dicyandiamide (SF+D) one, with the exception of the TET one, in which the SP+TR and SP+EP scores are slightly reduced, but not significantly.

The distribution of the environmental loads in the other three alternatives is not proportional, while in some impact categories the SF+SR is the best alternative (MET, HCT, HNCT), for others it is the most impactful (as is the case for GW, TET and FRS). The reason for the higher impact in those categories is mainly given by the need to use the epoxy resin, as well as by the higher amount of soybean meal required for the bio-adhesive formulation. On the other hand, with regard to SP+ER and SP+TR, for all the impact categories the environmental scores are quite similar, mostly equal, with the exception of HNCT, in which the SP+TR alternative implies a slightly higher load, and in the FRS one, in which, on the contrary, SP+ER presents the highest score.

In view of the results obtained and the discussion on the comparison of the soy bio-adhesive alternatives, it could be concluded that, from an environmental perspective, the SF+D scenario is the most attractive for the substitution of formaldehyde-based resins, given its low environmental impact compared to the other scenarios. However, the differences between the SP+ER, SF+ER and SR+TR alternatives are not as significant as those achieved with the SP+MA and SF+WP scenarios, so also these three bio-based adhesives could be categorized as suitable for such substitution.

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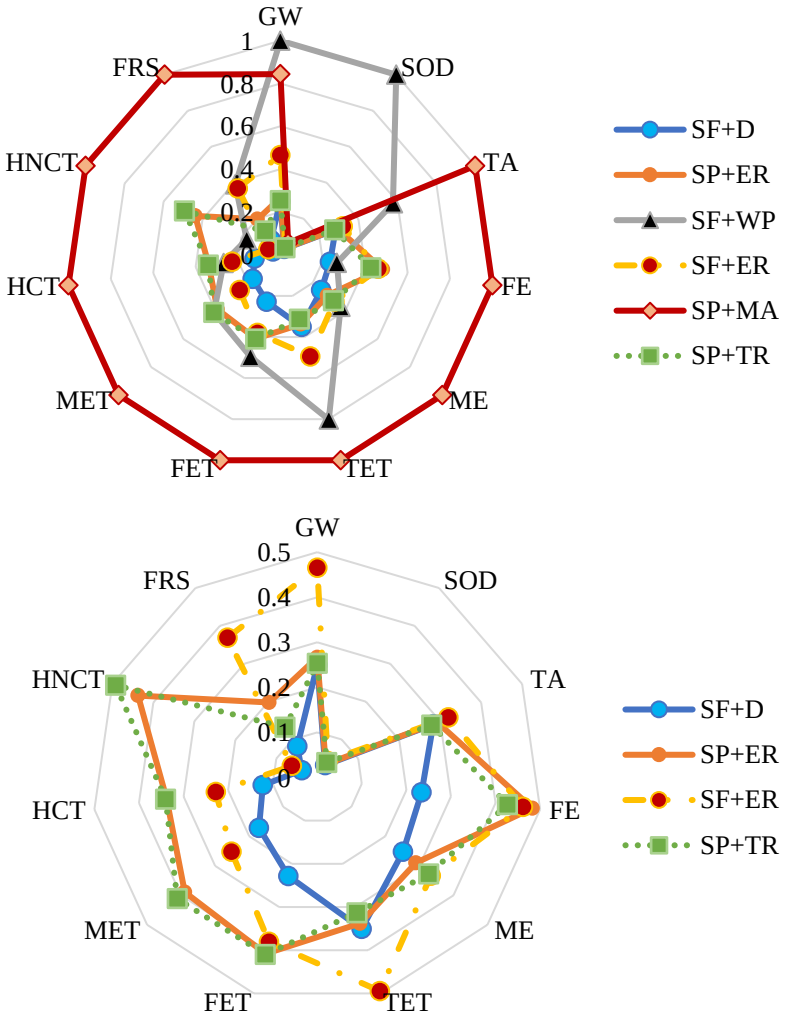

Figure 38. Comparative analysis of the soy bio-adhesives alternatives

6.6.2 Starch based bio-adhesives.

The impact results obtained after the environmental assessment have been used for the comparison of the four proposed starch-based bio-adhesive alternatives by applying the Recipe Midpoint calculation methodology. As can be seen in **Figure 39**, the starch bio-adhesive hydrolyzed with N-methyl acrylamide alternative has the highest potential environmental impact, being the most detrimental in most of the impact categories related to environmental quality. On the other hand, in the two specific categories of harm to human health, it is identified as the best alternative, since it has the least negative impact on health.

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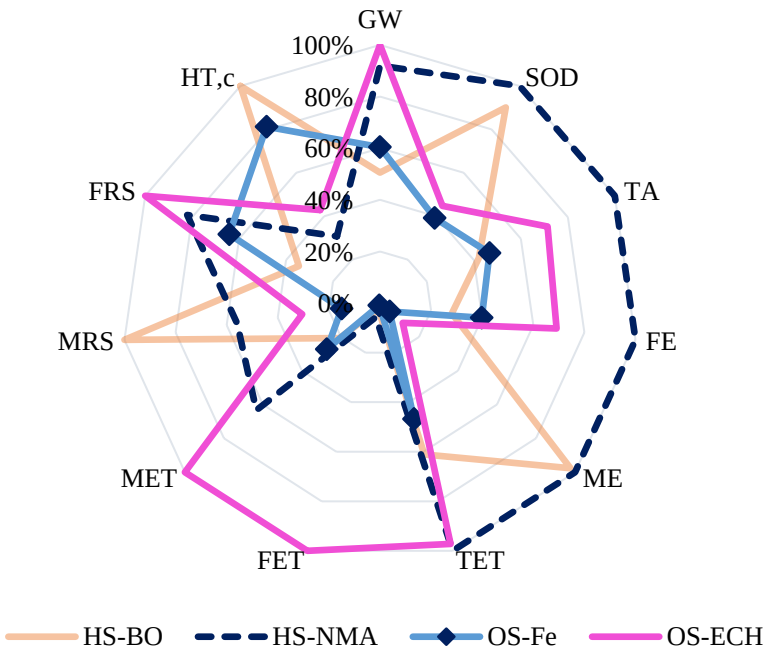

Figure 39. Comparative analysis of the starch bio-adhesives alternatives

The second worst alternative, from an environmental point of view, is the OS-ECH alternative (starch bio-adhesive oxidized with NaClO and ECH). In the ecotoxicity categories (FET, TET and MET), as well as in the GW and FRS categories, it presents the highest impact values compared to the other three. The reason for its high contribution in these categories is based on the use of EPR as a crosslinking agent. In addition to requiring a significant amount per kg of bio-adhesive produced (0.22 kg/kg), its production process is highly dependent on non-renewable fossil resources, and also uses certain chemical agents with a high potential for negative impact on environmental quality, resulting in significant environmental contributions.

The best results were obtained for the hydrolyzed starch alternatives, being hydrolyzed starch bio-adhesive with bio-oil (HS-BO) the most promising in most of the impact categories studied, with the exception of MRS, ME and HTC. The reason for its significant contribution to the MRS category stems from the energy requirements of the adhesive formulation process, which will involve significant consumption of non-renewable fossil resources. As for its impact in the ME category, it is a consequence of the emission of chlorinated compounds, since these emissions are higher than those of the other proposed bio-adhesive alternatives. Finally, in the HTNC impact category, the background activities associated with corn starch are the hotspot in this category. Since this second alternative has the highest ratio of starch/bio-adhesive of the four proposed alternatives (0.44:1), its environmental impact in this category is also the most significant.

The results obtained for OS-Fe alternative also show the high potential of this bio-adhesive from an environmental sustainability point of view, as its life cycle assessment has resulted in low impact values for most of the categories studied, except for HT_{nc}, where it is identified as second bio-adhesive alternative with the highest impact. The use of VAc and BAc in its formulation is what leads to the emerging toxicity of this third alternative. Therefore, one way to reduce its impact, and thus improve its quality and consider it a safe option for human health, would be to use other polymerization agents, such as PVA, which has shown low levels of impact in different environmental categories.

6.6.3 Comparison with synthetic resins

The scores obtained by the development of the ReCiPe Endpoint methodology are plotted in **Figure 40**. It should be mentioned that Ecoinvent database has been used for obtaining the damage scores for UF and PF synthetic resins, while for the MUF the data was obtained by using the research report developed by Silva et al. (2015) (Silva et al., 2015). As it could be appreciated, all the single damage scores obtained for the bio-based adhesives alternatives are lower to that of formaldehyde-based resins, being the alternatives of HS-NMA, OS-ECH and SP+MA, the ones closer to the formaldehyde alternative with the lower damage potential, the UF resin.

With respect to the starch scenarios, the one more promising are the hydrolyzed starch combined with bio-oil, as it is the alternative that provides the lowest damage potential. This feature is expected given the lowest environmental scores obtained when applying the ReCiPe MidPoint methodology. But the alternative of oxidation of starch OS-Fe is not as far, thus also considered as a good alternative for replacement.

In the case of the soy-based bio-adhesives, the difference is more notorious, being the SF+D alternative the best option, given its reduced damage score, amounting to 15, the lowest between all the adhesives under evaluation. Similar values are obtained for the SP crosslinked with tannin resin (SP+TR) and soy protein crosslinked with epoxy resin (SP+ER), accounting for 19 mPt and 20 mPt of damage, respectively. In general, it could be concluded that mostly all the soy bio-adhesives under evaluation, both using soybean meal and soy protein, are good candidates for replacing synthetic resins.

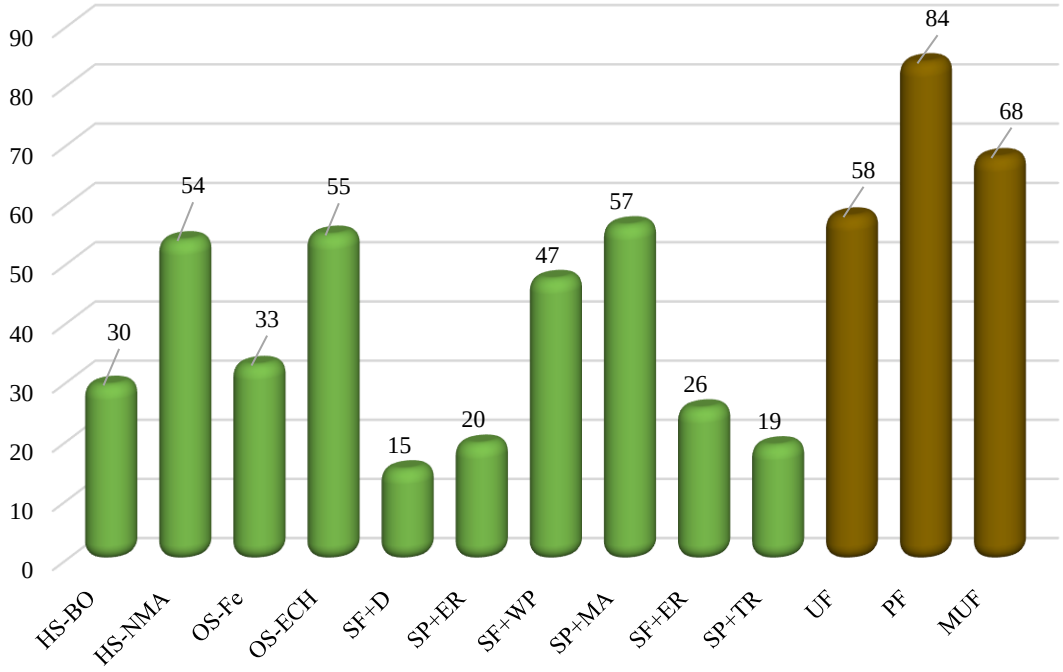

Figure 40. Comparative analysis of the soy and starch bio-adhesives alternatives with synthetic resins

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6.7 Main conclusions achieved.

This chapter has focused on the development of bio-based scenarios formulated with soy and starch. In the case of the soybean bioresource, two main generic alternatives have been considered: direct utilization of soybean meal for subsequent cross-linking with specific chemicals, or requirement of a pre-treatment stage for the extraction of proteins to be used for the bio-adhesive formulation. On the other hand, when evaluating starch, to allow its activation and functionalization, two main approaches have been evaluated, hydrolyzation and oxidation and then, as in the case of soybean, the performance of a cross-linking reaction to obtain the final formulated bio-adhesive.

Through the development of mass and energy balances, together with the use of the life cycle assessment methodology, all the evaluated scenarios were found to have a high potential for the substitution of synthetic resins, given their reduced environmental burden when evaluated through the ReCiPe EndPoint methodology. However, to improve the production scenarios and to move towards more sustainable bio-adhesives, certain identified hotspots should be further improved, being the reduction on the need of energy and the avoidance of "extra-dose" of crosslinking agents and chemicals the ones more significant.

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7

New environmental approach based on a combination of Planetary Boundaries and Life Cycle Assessment in the wood-based bio-adhesives market

This chapter partially reproduces content already published as "Arias, A., Feijoo, G., Moreira, M. T. (2022). New Environmental Approach Based on a Combination of Planetary Boundaries and Life Cycle Assessment in the Wood-Based Bioadhesive Market. *ACS Sustainable Chemistry & Engineering*, *10*(34), 11257-11272."

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SUMMARY

The Sustainable Development Goals defined by the United Nations established a roadmap on the way towards sustainability to achieve a paradigm shift in the status quo of production processes and services. In this context, the role of the bioeconomy based on the use of renewable resources but also on the valorization of bio-based waste could contribute to a higher degree of sustainability, as long as it is demonstrated that the related processes and products involve indicators that could represent an advantage with their competing counterparts. To this end, it is essential to apply a methodology that allows the assessment of environmental impacts and potential damages at a global level, being LCA the one selected.

In this regard, it is necessary to transform LCA impact scores to planetary boundary (PB) values, for which a threshold has been previously established. This has been the focus of this manuscript, in which the environmental sustainability ratios of different bio-adhesive scenarios have been evaluated under the combined framework of PBs and LCA for wood-based bio-adhesives following different allocation approaches, based on egalitarian, utilitarian and grandfathering principles. In this way it has been possible to assess the potential of bio-adhesives to avoid the use of synthetic resins in the wood-based panel production chain.

It is in this topic in which this **Chapter 7** is framed, in which an absolute sustainability assessment is carried out considering the potentiality of impact at planetary level. The scenarios under evaluation are the ones previously assessed on **Chapter 5** and **Chapter 6,** with the objective of identifying whether the proposed alternative bio-adhesives can be considered truly sustainable from an environmental point of view. In addition, an overall sustainability ratio is also provided, considering the three principles mentioned above and the values from the LCA assessment for their calculation.

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7.1 Going forward planetary levels

The mitigation of the environmental impact of anthropogenic activities is one of the main reasons for moving forward the current production models to the development of bio-based processes, basically biorefineries, considered drivers of change (Accorsi, 2019; Findler et al., 2019; Katakojwala and Mohan, 2021; Khan et al., 2021; Martin-Dominguez et al., 2018). The spotlight is on the circular economy concept, where the flow of materials is not based on "use and throw away" but on "use and reuse". However, the use of renewable resources or unusable flows from other productive sectors, such as agriculture or industry, does not always lead to a reduction of environmental impacts. This is often attributed to the lack of optimization of large-scale processes, as most new bio-based production models are developed on a laboratory or pilot scale.

The question arises as to how to determine the environmental impacts associated with production models, in order to assess not only the environmental damage, but also what improvement strategies should be carried out to reduce the environmental burden. For these assessments, the Life Cycle Assessment methodology is considered an essential and fundamental tool that report the environmental profile in terms of impact values grouped by categories(ISO, 2006). However, although the LCA methodology is considered an essential tool, its impact values are not capable of quantifying environmental damage in absolute sustainability references(Sala et al., 2020). In this approach, i.e., for the assessment of the globalization of an impact resulting from a production process or a product, it is necessary to combine the concept of planetary boundaries with that of LCA. In this way, an absolute sustainability study is carried out, which makes it possible to define, in a deeper way, whether a biotechnological biological process alternative can really be considered as environmentally sustainable.

The methodology integrating the combined application of LCA and PB$_S$ considers as an initial step the calculation of impacts according to the Environmental Footprint/ILCD guidelines. Subsequently, it is necessary to apply characterization factors, for which the inventory has to be evaluated once the impact result has been obtained, as only some substances apply for the PBs results. The results will be extrapolated to a planetary study level, so it is necessary to use allocation approaches and criteria that will be developed later on. Besides, this planetary assessment approach has been applied to analyze the environmental assessment of wood adhesives, both bio-based, i.e., those based on starch, soya, tannins and lignin, and synthetic ones, being urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-urea-formaldehyde (MUF).

7.2 From LCA to PBs framework: brief summary of the methodology

The methodology that is required to be developed has been previously defined and discussed on **Chapter 4** of this thesis dissertation. However, in order to give a brief summary for its development, a simple description is given. The methodology is developed in six main steps, the first three related to the LCA methodology, including the collection of the data, the selection of the calculation methodology, based in this case on the Environmental Footprint/ILCD recommendations guidelines, and the score of the environmental loads. Afterwards, if follows the transformation of the LCA values, per impact category, into PBs scores, for which each of the impact categories should be assessed deeply and, to the obtained values, applied a characterization factor in order to transform the LCAs into PBs scores. To this end, the sum up of all the individual contributors will give the final PB value, which is going to be compared with the earth limits, in order to assess whether those are surpassed or not.

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Besides, an allocation of the process scenarios is needed to be considered to evaluate those under a planetary level. Three main principles are used for the performance of the allocation on the evaluation of the scenarios, which considers the interrelation between environmental, economic and social frameworks (Hjalsted et al., 2021; López-Linares et al., 2021). In the case of the utilitarian principle, the combination of economic and social pillar is considered by the population amount, the gross value added (GVA) and the final consumption expenditure (FCE) parameters of a particular region. The main objective is to maximize the welfare of the social community through the insurance of economic stability.

For the egalitarian principle, the integration of the environmental pillar is considered in combination with the social one, as it is based on the hypothesis that all the environmental burdens should be distributed over the population, in an "equal per capita basis" (E.A. Perdomo Echenique et al., 2022). Lastly, for the case of the grandfathering principle, it is mainly based on the environmental pillar, considering the GHG emissions as main factor for the evaluation of the alternatives, by the assessment of the associated impacts at both industrial and sectoral levels of production (Damon et al., 2020).

It should be mentioned that the allocation shares considered in the development of this study were initially focused on the European level, given the potential of the timber sector in Europe and the availability of data at both continental and sectoral levels in terms of production, imports, exports and economic statistics (GVA and FCE) and greenhouse gas (GHG) emissions. On the other hand, after assessing sectoral data, the data provided from the Food and Agriculture Organization of the United Nations (FAOSTAT), the World Bank Open Data (World Bank Open Data, 2023) and the Emission Database for Global Atmospheric Research (European Environment Agency, EDGAR) has been used as databases for the performance of the assessments.

By the evaluation of those databases, it was identified that Sweden has one of the highest GVA values in Europe, while standing out for its low GHG emissions, so this nation has been chosen to assess the results of the allocation shares at a lower level. Furthermore, in order to provide an intermediate allocation value, Spain has been chosen as another study scenario, because it has an intermediate GVA value, but, compared to Sweden, higher annual GHG emission values. In this way, a compendium of impact results and various environmental sustainability ratios is presented, which provides a comprehensive and global view of the potential degrees of sustainability of each of the allocation factors considered.

On the other hand, it is important to note that the proposed bio-adhesive scenarios are based on large-scale process simulation performed on the basis of laboratory data available in the literature. In contrast, the synthetic resin scenarios, which are widely used in the wood-based panel production sector, are evaluated using data obtained from large-scale production processes, whose production parameters are fully optimized. This implies that the degree of improvement of bio-adhesive scenarios is extensive, and much more significant than in the case of synthetic resins, where the degree of optimization is very low or almost non-existent. Therefore, those bio-based adhesive scenarios that have a lower ratio of environmental sustainability (R_{ES}) value than synthetic resins propose a production scenario with a much higher degree of sustainability, given their wide feasibility of improvement.

7.3 Scenarios under evaluation

As mentioned previously, the focus of the PBs evaluation is based on the environmental profiles of various scenarios of bio-based adhesives applied to wood-based panel production, using the LCA methodology. While these results provide the potential

and degree of sustainability from an attributional scope, they do not show how this new bio-based process scenario can affect the environment in a planetary approach. Therefore, it is interesting to extend the LCA values to a global level, i.e., to transform from an attributional model to a consequential model, using the principles and knowledge of the planetary boundary concept.

For this purpose, the proposed scenarios for the assessment under a consequential model perspective are represented in **Table 24**, together with the literature reference where the description of the production processes and the inventory can be found. It is important to mention that, for this study, the Environmental Footprint recommendations (European Commission, 2021) have been considered in the selection of the calculation methodologies for each of the impact categories, therefore, the environmental damage values for each of the scenarios have been recalculated based on the inventory data included in the aforementioned bibliographic references.

Table 24. Scenarios for reporting the PBs values from previous environmental bio-adhesives assessments.

Bio-adhesive	Definition	Reference
KL-NIPU	Kraft Lignin Non-Isocyanate Polyurethane	(Arias et al., 2022)
OSL-NIPU	Organosolv Lignin Non-Isocyanate Polyurethane	(Arias et al., 2022)
SPI-NIPU	Soy Protein Isolate Non-Isocyanate Polyurethane	(Arias et al., 2022)
T-NIPU	Tannin Non-Isocyanate Polyurethane	(Arias et al., 2022)
HS-BO	Hydrolyzed Starch with Bio-Oil	(Arias et al., 2021a)
HS-NMA	Hydrolyzed Starch with N-methylol Acrylamide	(Arias et al., 2021a)
OS-Fe	Oxidized Starch with $FeSO_4$ and H_2O_2	(Arias et al., 2021a)
OS-ECH	Oxidized Starch with NaClO and Epichlorohydrin	(Arias et al., 2021a)
TG	Tannin from bark crosslinked with glyoxal	(Arias et al., 2021c)
TH	Tannin from bark crosslinked with hexamine	(Arias et al., 2021c)
TP	Tannin from bark crosslinked with p-formaldehyde	(Arias et al., 2021c)
TNA	Tannin from bark crosslinked with $NH_4(OH)$	(Arias et al., 2021c)
TNH	Tannin from bark with Hexamethylenediamine	(Arias et al., 2021c)
SF-D	Soybean meal crosslinked with Diacyandiamide	(Arias et al., 2021b)
SF-WP	Soybean meal crosslinked with w-Polyurethane	(Arias et al., 2021b)
SF-ER	Soybean meal crosslinked with SBDS and epoxy resin	(Arias et al., 2021b)
SP-EP	Soy Protein crosslinked with Polyacrylamide	(Arias et al., 2021b)
SP-MA	Soy Protein crosslinked with Maleic Anhydride	(Arias et al., 2021b)
SP-TR	Soy Protein crosslinked with Tannin Resin	(Arias et al., 2021b)
Synthetics	Urea/Phenol/Melamine Urea Formaldehyde	(Silva et al., 2015; Yang and Rosentrater, 2020)

Once the scenarios under evaluation are selected, it is important to mention that one of the main objectives in the calculation of environmental shares using the allocation principles is to determine the degree of environmental sustainability of the proposed production scenarios, denoted as R_{ES}. It is measured as the ratio between the PB-LCA value calculated for each of the planetary boundaries and the proposed adhesive

production scenarios, and the $aSOS_{pp}$ (Safe Operating Space), where pp is the type of allocation and the principle used for its calculation (Enrique Alejandro Perdomo Echenique et al., 2022). The value of this ratio will be indicative of the degree of sustainability of the production scenario. Thus, if the R_{ES} score is equal to or less than 1, then the scenario is considered environmentally sustainable, while if it is greater than 1, it means that the scenario is unsustainable, as the environmental load exceeds the established PB limit, and therefore requires optimization and improvement (Bjørn et al., 2015; Fang et al., 2015).

Therefore, the lower the R_{ES} score, the gross difference between the actual PB-LCA value and the allocated safe operating space, the higher the absolute environmental sustainability potential of the scenario under assessment. So, in this sense, the scenarios with the lowest R_{ES} scores are the ones that are classified as the best production strategies under the PB approach. Thus, all scenarios proposed in **Table 24** will be analysed considering the allocation principles considered, expressing their environmental damage using the R_{ES} approach.

7.4 Planetary boundaries of wood bio-based adhesives: a global approach

When considering the assessment of the process scenarios in global terms, the planetary values are expected to be considerably low compared to the established PB limit values. That is why these scores have been used to evaluate the scenarios comparatively, i.e., between bio-based adhesives and synthetic resins. In this sense, the potential of bio-based adhesives has been established from the point of view of environmental sustainability and impact reduction. In this methodological approach, the numerical results of the planetary boundary values are included in **Tables 25** and **26**. Furthermore, comparative graphs showing the impact values on a scale between 0 and 1 are included, applying the value of 1 to the adhesive alternative, both bio-based and synthetic, with the highest impact value, for each of the planetary boundaries under assessment categories

Table 25. PBs scores for each adhesive scenario: climate change energy imbalance, atmospheric CO_2 concentration and ocean acidification.

Bio-Adhesive	$PB_{CC,imb}$	$PB_{CC,CO2}$	PB_{OA}	Bio-Adhesive	$PB_{CC,imb}$	$PB_{CC,CO2}$	PB_{OA}
	W/m^2	ppm	Ω_{arag}		W/m^2	ppm	Ω_{arag}
KL-NIPU	$8.36 \cdot 10^{-4}$	$2.12 \cdot 10^{-2}$	$1.73 \cdot 10^{-5}$	TP	$9.78 \cdot 10^{-4}$	$2.17 \cdot 10^{-2}$	$1.00 \cdot 10^{-5}$
OSL-NIPU	$3.30 \cdot 10^{-4}$	$1.05 \cdot 10^{-2}$	$1.61 \cdot 10^{-5}$	TNA	$2.43 \cdot 10^{-3}$	0.13	$3.48 \cdot 10^{-4}$
SPI-NIPU	$7.81 \cdot 10^{-4}$	1.77	$8.73 \cdot 10^{-6}$	TNH	$1.01 \cdot 10^{-3}$	$4.65 \cdot 10^{-2}$	$1.13 \cdot 10^{-4}$
T-NIPU	$1.00 \cdot 10^{-3}$	$4.07 \cdot 10^{-2}$	$2.47 \cdot 10^{-5}$	SF-D	$1.50 \cdot 10^{-4}$	1.36	$2.66 \cdot 10^{-6}$
HS-BO	$7.83 \cdot 10^{-4}$	0.62	$1.14 \cdot 10^{-4}$	SF-WP	$2.24 \cdot 10^{-4}$	0.83	$2.43 \cdot 10^{-6}$
HS-NMA	$3.25 \cdot 10^{-4}$	0.59	$2.46 \cdot 10^{-6}$	SF-ER	$3.81 \cdot 10^{-3}$	2.19	$6.49 \cdot 10^{-6}$
OS-Fe	$1.65 \cdot 10^{-4}$	$3.86 \cdot 10^{-3}$	$2.62 \cdot 10^{-6}$	SP-EP	$4.79 \cdot 10^{-4}$	1.30	$6.54 \cdot 10^{-6}$
OS-ECH	$3.24 \cdot 10^{-4}$	$1.32 \cdot 10^{-2}$	$5.70 \cdot 10^{-6}$	SP-MA	$2.17 \cdot 10^{-4}$	1.97	$5.92 \cdot 10^{-6}$
TG	$9.96 \cdot 10^{-4}$	$2.21 \cdot 10^{-2}$	$1.03 \cdot 10^{-5}$	SP-TR	$2.47 \cdot 10^{-4}$	0.93	$2.39 \cdot 10^{-6}$
TH	$1.00 \cdot 10^{-3}$	$2.23 \cdot 10^{-2}$	$1.05 \cdot 10^{-5}$				
Synthetics	$3.35 \cdot 10^{-4}$	$4.47 \cdot 10^{-2}$	$7.09 \cdot 10^{-5}$	Synthetics	$3.35 \cdot 10^{-4}$	4.47	$7.09 \cdot 10^{-5}$
PB limit	**1**	**350**	**2.75**	**PB limit**	**1**	**350**	**2.75**

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Table 26. PBs scores for each adhesive scenario: atmospheric aerosol loading, stratospheric ozone depletion and biogeochemical flows.

Adhesive	PB_{AAL}	PB_{SOD}	$PB_{BF,N}$	$PB_{BF,P}$
	AOE	DU	Tg N/year	Tg P/year
KL-NIPU	$2.78 \cdot 10^{-5}$	$6.64 \cdot 10^{-5}$	0.05	$5.29 \cdot 10^{-4}$
OSL-NIPU	$1.24 \cdot 10^{-5}$	$5.04 \cdot 10^{-5}$	0.03	$4.77 \cdot 10^{-4}$
SPI-NIPU	$2.80 \cdot 10^{-5}$	$7.05 \cdot 10^{-5}$	0.05	0.17
T-NIPU	$2.90 \cdot 10^{-4}$	$1.35 \cdot 10^{-4}$	0.16	$2.75 \cdot 10^{-3}$
HS-BO	$7.10 \cdot 10^{-6}$	$1.05 \cdot 10^{-5}$	0.03	$6.27 \cdot 10^{-2}$
HS-NMA	$7.80 \cdot 10^{-6}$	$1.11 \cdot 10^{-5}$	0.04	$1.11 \cdot 10^{-2}$
OS-Fe	$9.34 \cdot 10^{-6}$	$2.13 \cdot 10^{-4}$	0.02	$1.67 \cdot 10^{-3}$
OS-ECH	$1.69 \cdot 10^{-5}$	$3.92 \cdot 10^{-5}$	0.04	$5.60 \cdot 10^{-3}$
TG	$3.01 \cdot 10^{-5}$	$3.10 \cdot 10^{-5}$	0.05	$8.80 \cdot 10^{-5}$
TH	$3.09 \cdot 10^{-5}$	$4.02 \cdot 10^{-5}$	0.05	$1.17 \cdot 10^{-4}$
TP	$2.97 \cdot 10^{-5}$	$3.24 \cdot 10^{-5}$	0.05	$4.37 \cdot 10^{-4}$
TNA	$2.94 \cdot 10^{-5}$	$7.03 \cdot 10^{-5}$	0.05	$3.97 \cdot 10^{-3}$
TNH	$2.66 \cdot 10^{-5}$	$5.36 \cdot 10^{-5}$	0.05	$1.37 \cdot 10^{-3}$
SF-D	$5.15 \cdot 10^{-5}$	$2.14 \cdot 10^{-5}$	0.01	$3.23 \cdot 10^{-2}$
SF-WP	$7.24 \cdot 10^{-5}$	$4.08 \cdot 10^{-6}$	0.01	$7.75 \cdot 10^{-2}$
SF-ER	$1.02 \cdot 10^{-5}$	$1.12 \cdot 10^{-5}$	0.02	$5.17 \cdot 10^{-2}$
SP-EP	$1.76 \cdot 10^{-5}$	$5.11 \cdot 10^{-5}$	0.03	0.12
SP-MA	$6.87 \cdot 10^{-6}$	$7.57 \cdot 10^{-6}$	0.01	$4.85 \cdot 10^{-2}$
SP-TR	$7.31 \cdot 10^{-6}$	$4.47 \cdot 10^{-6}$	0.01	$8.70 \cdot 10^{-2}$
Synthetics	$2.05 \cdot 10^{-5}$	$5.49 \cdot 10^{-5}$	0.07	$2.85 \cdot 10^{-3}$
PB limit	0.25	275	62	11

7.4.1 Isocyanate-free (NIPU) bio-adhesives

Figure 41 shows the planetary impact scores for isocyanate-free bio-adhesives produced using lignin, both Kraft (KL-NIPU) and Organosolv (OSL-NIPU), tannins (T-NIPU) and soy (SPI-NIPU) as renewable-based raw materials, and their respective comparison with synthetic resins. It is worth mentioning that the value of formaldehyde-based resins has been calculated individually for UF, PF and MUF adhesives, as they are the most prominent in panel boards, and then, considering their overall production value, a single planetary limit value for non-renewable based resins is obtained. As can be seen, the environmental implication is diverse among the PBs under discussion, the contribution values of the synthetic-based resins are those represented in red, while those of the bio-based resins are in green.

For all NIPU bio-adhesive alternatives, the contribution on the $PB_{CC,imb}$ is significant, being higher than 50% compared to the synthetic resins, except for the OSL-NIPU bio-adhesive, where its impact value is analogous to that of the formaldehyde-based resins. In contrast, in the planetary categories of ocean acidification (OA) and biogeochemical flows, both in nitrogen ($PB_{BF,N}$) and phosphorous ($PB_{BF,P}$) cycles, the environmental damage resulting from the production of NIPU bio-adhesives is significantly lower compared to that of formaldehyde resins. Only one exception is the contribution of SPI-NIPU resin production in $PB_{BF,P}$, where it is 20% higher compared to synthetic resins. In the other PBs the variability of the damage depends on the type of bio-adhesive. However, in seeking to establish which of the alternatives is the most beneficial option from an environmental sustainability point of view, i.e., the one that results in a lower degree of impact and therefore contributes to keeping environmental loads below the established planetary boundaries, the preferred alternative would be OSL-NIPU. KL-NIPU could also be considered as a suitable option, but its implication on the $PB_{CC,imb}$ planetary boundary is considerably higher compared to that of the OSL-NIPU bio-adhesive scenario.

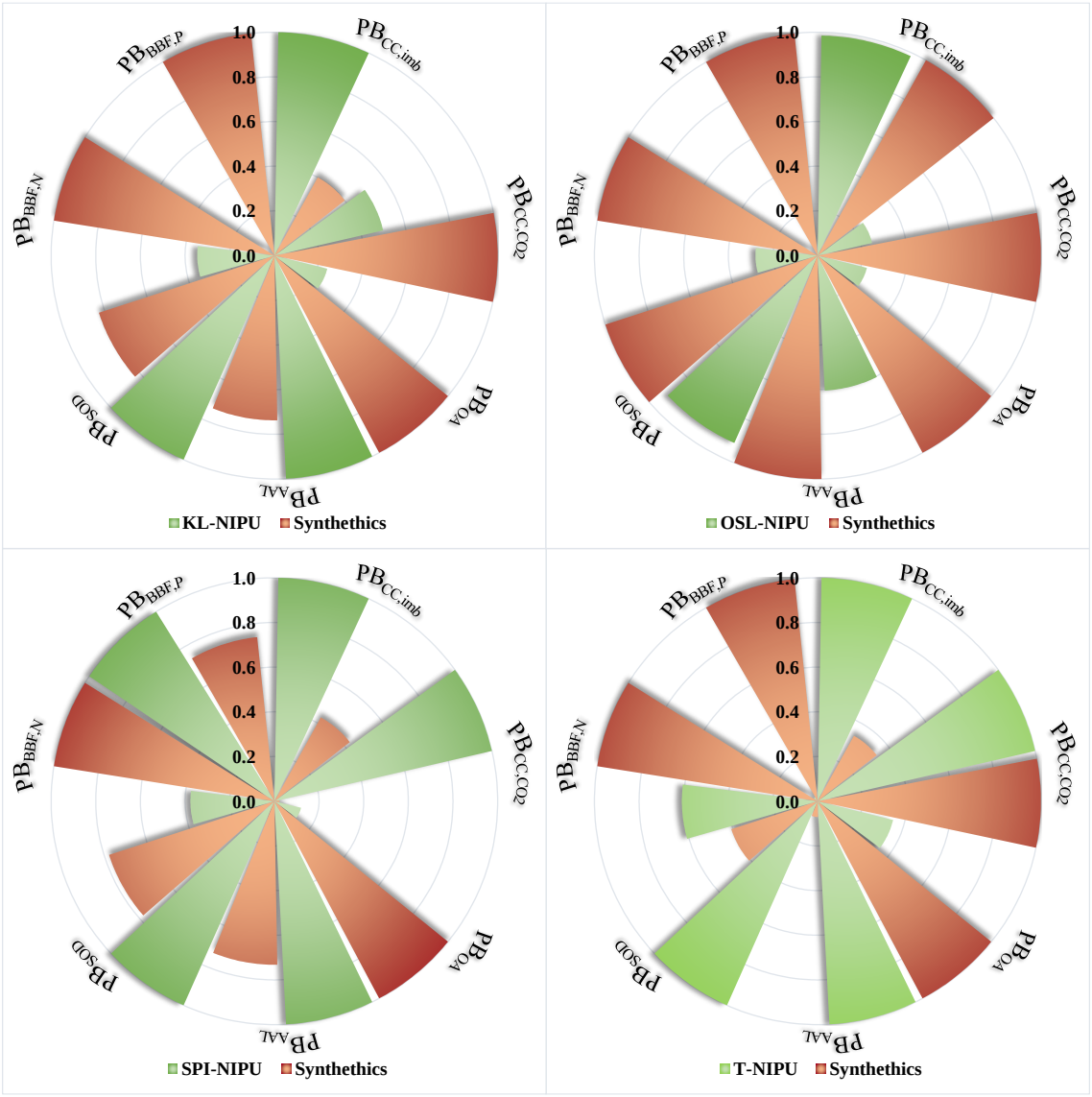

Figure 41. Planetary impact scores comparison between isocyanate-free bio-adhesives and synthetic resins

7.4.2 Starch-based bio-adhesives

Starch-based bio-adhesives are another type of bio-adhesives that have been studied for the replacement of formaldehyde-based resins. Their potential is high due to the mechanical and thermogravimetric properties derived from the use of starch polymers, characterized by the ability to provide adequate bonding forces to produce wood-based panels, ensuring an adhesive-board bond that meets the standards and criteria requirements for consumer use (Moubarik et al., 2010b). However, in the approach to studying their cost-effectiveness, it is also important to consider their degree of sustainability and environmental suitability. **Figure 42** shows the PB values obtained for these bio-adhesives.

A significant impact of bio-adhesives in the $PB_{CC,imb}$ category compared to the environmental burden of synthetic resins is observed, being significantly higher for the starch-oil and starch-Fe scenarios, but quite similar in the cases of starch-N and starch-ECH, which shows their potential. On the other hand, it is observed that the alternatives

requiring starch oxidation for the bio-adhesive formulation, i.e., the starch-Fe and starch-EOH scenarios, result in a higher environmental burden in the stratospheric ozone depletion impact category associated with the PB_{SOD} planetary boundary, being much more significant for the starch-Fe scenario. However, a holistic assessment of the proposed bio-adhesive scenarios shows that their implication on the planetary boundaries is lower than that of synthetic resins in most of the analysed categories and, when compared to the previous bio-adhesive category, a higher potential of starch-based bio-adhesives is observed, given their lower contribution to the environmental burdens of the respective planetary boundaries. On the other hand, looking for the identification of the best scenario for this second category of bio-adhesives, it is established that starch-Fe bio-adhesive is the best alternative, although some improvement would be required to reduce its contribution to the PB_{SOD}.

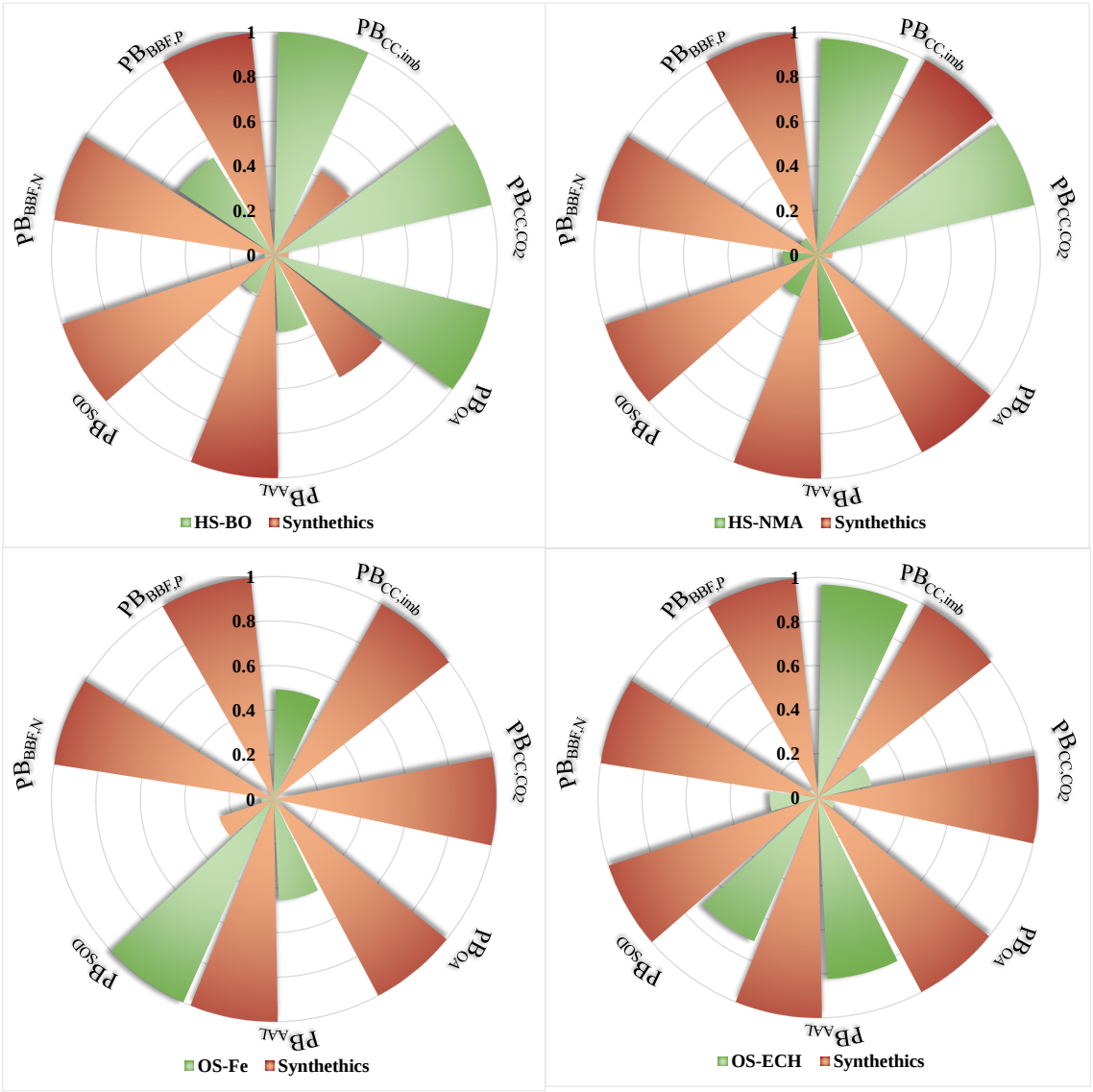

Figure 42. Planetary impact scores comparison between starch bio-adhesives and synthetic resins

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7.4.3 Tannin-based bio-adhesives

Research on tannin bio-adhesives has increased in recent years, its motivation derives from three main factors, firstly its wide availability and renewable nature, secondly its easy handling in bio-adhesive formulation, as it does not require as intensive an activation process as in the case of lignin, and thirdly, perhaps the most relevant, due to the superior performance of the final panel on which it is applied, as it provides highly competitive properties with those provided by formaldehyde-based resins (Chen et al., 2020a; Gonultas, 2018).

When assessing their environmental performance at the planetary level, it is observed that, while some alternatives appear to be suitable for reducing damage contributions in the PB values, given their lower scores obtained compared to those of synthetic resins, others lead to increased impacts, resulting in a lower potential for sustainability. This is the case for dimethyl carbonate (DMC) and hexamethylene diamine (HDMA) crosslinked tannin bio-adhesives, as shown in **Figure 43**. Even their involvement in PBs associated with biogeochemical nitrogen and phosphorus fluxes is almost zero, in the remaining categories their score is significantly higher compared to that of formaldehyde-based adhesives. In contrast, the potential of the other alternatives for tannin bio-adhesives is high, although some optimization would be required to try to decrease the impact on the $PB_{CC,imb}$ and PB_{AAL} categories. The main reason for the high impact value obtained in the PB_{AAL} is the background activities required for the manufacture of condensed tannins, including not only the extraction stage, but also the activities associated with forestry operations and waste stream management.

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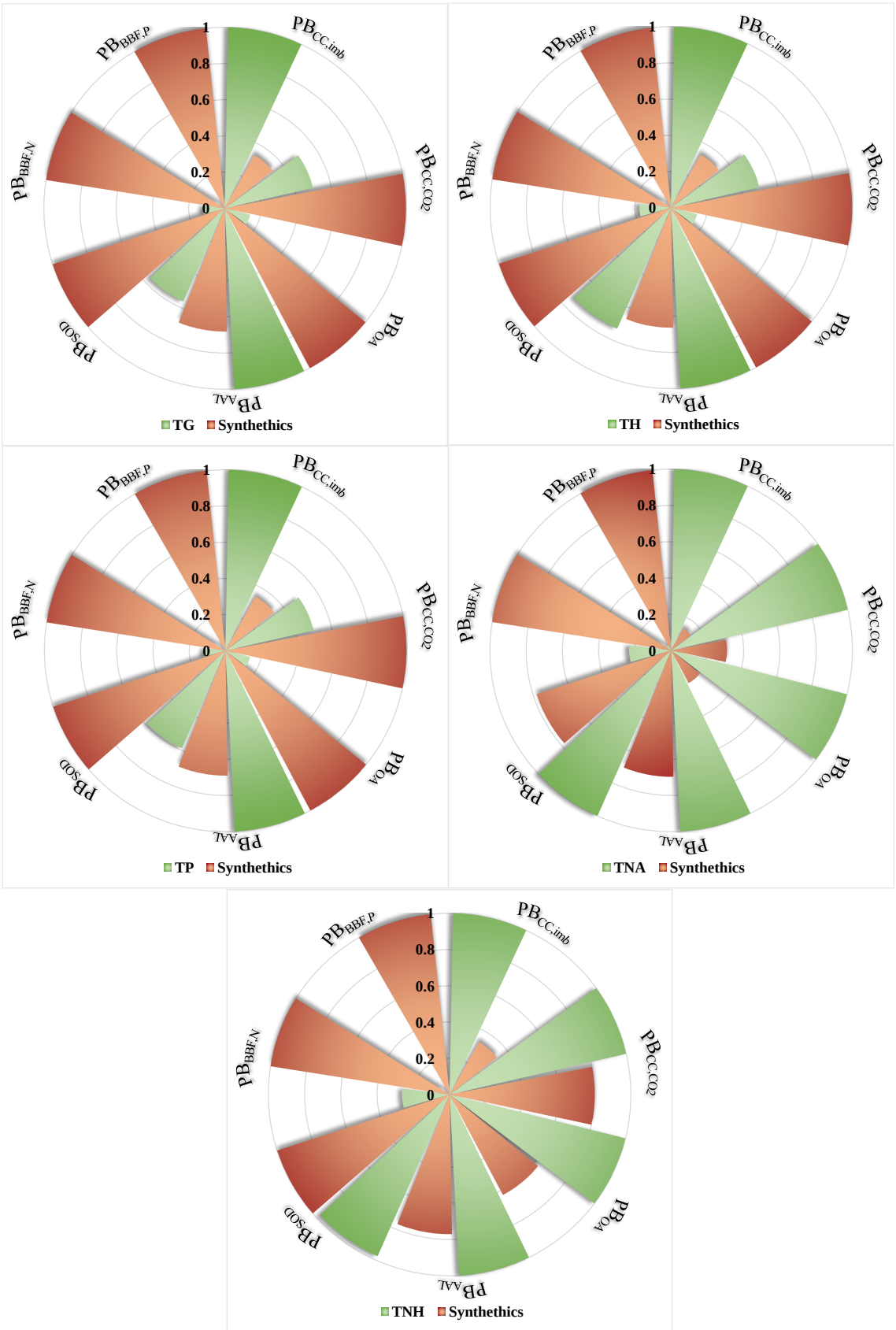

Figure 43. Planetary impact scores comparison between tannin bio-adhesives and synthetic resins

7.4.4 Soy-based bio-adhesives

The environmental loads of soy-based bio-adhesives under a LCA approach were assessed on **Chapter 6**, in which it has been reported that the main hotspot is the soy protein extraction stage (Arias et al., 2021b). Its impact is based on two main causes: the energy requirements needed for soy protein extraction and the secondary activities associated with agricultural cultivation and harvesting. Regarding its assessment on a planetary level, the contribution in the categories associated with climate change, i.e., $PB_{CC,imb}$ and $PB_{CC,CO2}$, is also significant, and higher than for formaldehyde-based resins in most of the proposed scenarios.

In the case of $PB_{CC,imb}$, all soy bio-adhesive alternatives have a contribution that far exceeds that of synthetic resins. The main reason for this high environmental burden probably stems from the electricity consumption and heat requirements, mostly obtained from fossil resources, as well as the lack of optimization and energy efficiency of the soy protein extraction and adhesive production processes. Furthermore, for $PB_{CC,imb}$ it is also observed that formaldehyde-based resins have a lower damage score, which leads to consider them as more suitable options from a sustainability point of view. However, when assessing the categories of biogeochemical flows and the impact over the stratospheric ozone depletion planetary boundary, the selection of bio-based adhesives is preferable, as their damage burden is almost zero compared to that of synthetic ones.

Considering that preserving the natural cycling of nitrogen and phosphorus compounds are essential for crop development, for the survival of organisms given their involvement in the food value chain, for the productivity of ecosystems and to avoid the accumulation of harmful toxic compounds in soil, air and water, the development of wood adhesive alternatives that contribute to maintaining the natural cycling of these nutrients is essential (Aczel, 2019; Weathers et al., 2016). As **Figure 44** shows, the contribution of soy bio-adhesives in these PBs is negligible compared to that of formaldehyde adhesives, thus making them suitable options. However, to avoid potential damage to the remaining PBs, their optimization and process improvement is required, which is possible because their production alternatives are at an earlier stage of development compared to UF, MUF and PF resins, whose processes are fully developed and optimized.

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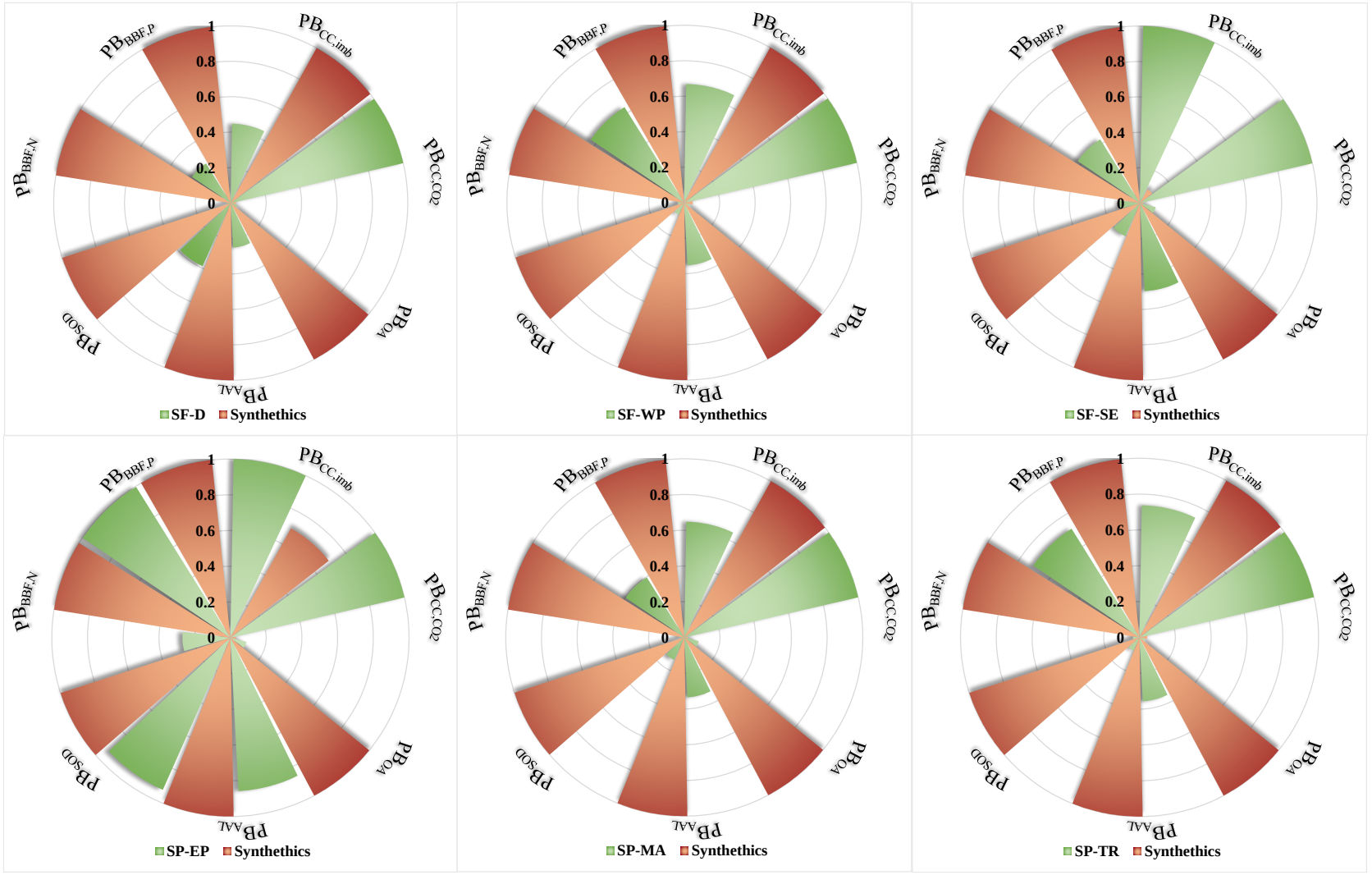

Figure 44. Planetary impact scores comparison between soy bio-adhesives and synthetic resins

7.5 Downscaling planetary boundaries

7.5.1 Utilitarian principle for allocating the PBs scores.

When assessing the total economy of the nation, one of the fundamental aspects to consider is the value of the Gross Domestic Product (GDP), as it expresses the size of the economy and how it performs. It is commonly used as a parameter to assess the overall "health" of the economy: the higher the GDP, the higher the performance of the economy is developing, indicating the economic sustainability of a nation/country (Slesnick, 2020). To this end, in calculating this score, three main approaches could be considered: production, income and expenditure approaches (Amal, 2016). The most common is the production approach, the income approach and the expenditure approach. The most common is the production approach, using GVA, the Gross Value Added, which is measured as the difference between the production values of the industry and the intermediate inputs needed in the production process (Miroudot and Ye, 2022). In this case, the industrial sector being assessed is the wood sector, specifically the one in charge of producing wood-based panels. In order to determine the sustainability index according to the GVA allocation approach, it is first necessary to calculate the allocated safe operating space (aSOS) for the communities of Europe, Sweden and Spain, based on the industrial and population scope (POP), $aSOS_{FCE,\ ind+POP}$. For this purpose, GVA and POP values were taken from the available database, being FAO (Food and Agriculture Organization of the United Nations)("FAOSTAT. Food and Agriculture Organization of the United Nations," n.d.), UNECE (United Nations Economic Commission for Europe) ("Statistical Database - United Nations Economic Commission for Europe," n.d.) and World Bank Group- International Development, Poverty & Sustainability ("World Bank Open Data | Data," n.d.). The data collected for the estimation of $aSOS_{GVA}$ are shown in **Table 27**, both for the territories of Europe, Sweden and Spain.

Table 27. GVA, POP and aSOS values at the European, Sweden and Spanish levels.

GVA_{WS}	$1.64 \cdot 10^{5}$	$4.09 \cdot 10^{3}$	$1.11 \cdot 10^{3}$
$GVA_{R/C}$	$1.13 \cdot 10^{7}$	$3.82 \cdot 10^{5}$	$9.97 \cdot 10^{5}$
$POP_{R/C}$	$7.48 \cdot 10^{8}$	$1.02 \cdot 10^{8}$	$4.67 \cdot 10^{8}$
$aSOS_{GVA,\ ind+POP}$	$1.40 \cdot 10^{-3}$	$1.24 \cdot 10^{-4}$	$6.76 \cdot 10^{-5}$

As can be seen in **Table 27**, the GVA value in the wood sector in Sweden is four times higher compared to that of Spain, but when it comes to country, Spain becomes the leader, with a value that is $6.15 \cdot 10^{5}$ times higher. Using these data, the allocated GVA safe operating space, $aSOS_{GVA}$, is estimated for the territories of Europe, Sweden and Spain, acquiring the lowest value for Spain and the highest for Europe, as expected. These values will directly affect the environmental sustainability ratio, R_{ES}, of the assessed wood bio-adhesives. As it is calculated by dividing the PB value, according to the impact scores obtained using the LCA methodology, by the $aSOS_{GVA}$, the lower the assigned score, the higher the R_{ES}, as it is inversely proportional. Seeking to assess the scenarios within the actual allocation approach, **Tables 28, 29 and 30** are depicted, corresponding to the European, Sweden and Spanish territories.

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Table 28.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{GVA}$, at European level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	0.60	0.21	0.02	$3.16 \cdot 10^{-3}$	0.18	0.60	0.06
OSL-NIPU	0.24	0.10	0.02	$2.40 \cdot 10^{-3}$	0.08	0.38	0.05
SPI-NIPU	0.56	17.54	0.01	$3.35 \cdot 10^{-3}$	0.18	0.61	18.96
T-NIPU	0.71	0.40	0.03	$6.42 \cdot 10^{-3}$	1.88	1.84	0.32
HS-BO	0.56	0.21	0.12	$4.99 \cdot 10^{-4}$	0.05	0.29	7.21
HS-NMA	0.23	5.84	$2.58 \cdot 10^{-3}$	$5.28 \cdot 10^{-4}$	0.05	0.49	1.28
OS-Fe	0.12	0.04	$2.75 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$	0.06	0.22	0.19
OS-ECH	0.71	0.13	0.01	$1.86 \cdot 10^{-3}$	0.11	0.45	0.64
T-G	0.71	0.22	0.01	$1.47 \cdot 10^{-3}$	0.20	0.55	0.01
T-H	0.71	0.22	0.01	$1.91 \cdot 10^{-3}$	0.20	0.61	0.01
T-P	0.70	0.22	0.01	$1.54 \cdot 10^{-3}$	0.19	0.55	0.05
T-NA	1.73	1.31	0.36	$3.34 \cdot 10^{-3}$	0.19	0.58	0.46
T-NH	0.72	0.46	0.12	$2.55 \cdot 10^{-3}$	0.17	0.59	0.16
SF-D	0.11	13.43	$2.79 \cdot 10^{-3}$	$1.02 \cdot 10^{-3}$	0.03	0.06	3.71
SF-WP	0.16	8.18	$2.55 \cdot 10^{-3}$	$1.94 \cdot 10^{-4}$	0.05	0.09	8.91
SF-ER	2.72	21.68	0.01	$5.32 \cdot 10^{-4}$	0.07	0.21	5.94
SP-EP	0.34	12.92	0.01	$2.43 \cdot 10^{-3}$	0.11	0.39	13.96
SP-MA	0.15	19.48	0.01	$3.60 \cdot 10^{-4}$	0.04	0.11	5.57
SP-TR	0.18	9.24	$2.51 \cdot 10^{-3}$	$2.12 \cdot 10^{-4}$	0.05	0.09	10.01
Synthetic	0.24	0.44	0.07	$2.61 \cdot 10^{-3}$	0.13	0.80	0.33
R_{ES}	1	1	1	1	1	1	1

At the European level (**Table 28)**, most of the sticker scenarios are below the threshold value for environmental sustainability, although there are some exceptions for certain PB categories. Those where the threshold value is exceeded for several bio-adhesive alternatives are $PB_{CC,ppm}$ and $PB_{BBF,P}$. This is particularly the case for SPI-NIPU bio-adhesives, starch-oil, starch-Fe and, as far as bio-adhesives formulated from soy are concerned, none of them are below the threshold value in the above-mentioned PBs. Therefore, in this first analysis, considering an allocation by GVA, it could be determined that soy-based adhesives should be formulated with another formulation method, or their production processes require significant optimization focusing on their main hotspots, which were identified by Arias et al. (2021) (Arias et al., 2021b).

In this aforementioned article, it was concluded that the main contributors to environmental burdens are the raw material itself, i.e., soybean, derived from agricultural activities (cultivation, fertilization, harvesting, etc.) and also the use of certain crosslinking agents (such as DMC or HDMA). On the other hand, when soy protein is used, thus requiring pre-processing of its extraction, it was identified that electricity consumption is also responsible for a significant impact on the environmental profile obtained. As for SPI-NIPU bio-adhesives, their lower environmental sustainability compared to their counterparts stems from the same reasons as those stated for soy-based adhesives: background agricultural activities together with the use of HMDA as crosslinking agents (Arias et al., 2022), although some contribution of power requirements, necessary for reactor agitation, is also observable in the environmental profile of this alternative.

Finally, in the case of starch, the bio-adhesive formulated with bio-oil requires an acid-hydrolysis pre-treatment of the starch, while the bio-adhesive formulated with iron sulphate, starch-Fe, is obtained with a starch oxidation pre-treatment. Regarding the environmental profile of the starch-oil bio-adhesive, the agricultural activities of cultivation and harvesting, together with the energy requirements and emissions associated with the production process, mainly ammonium sulphate and ammonium chloride, are the cause of its environmental score. In contrast, for the starch-Fe scenario, the chemicals required for polymerization and formulation of the bio-adhesive structure, butyl acrylate and vinyl acetate, are the inventory items that have resulted in higher impact value (Arias et al., 2021a).

On the other hand, when the allocation is done at the national level, for both Sweden (**Table 29**) and Spain (**Table 30**), most bio-adhesives, and even synthetic resins, exceed what is considered to be the environmental sustainability threshold value, with a single exception, the category of PB_{SOD}, in which all remain within the environmental threshold values. However, certain exceptions of sustainable bio-adhesives scenarios are noted in some of the PBs under assessment: PB_{OA}, $PB_{BF,P}$ and PB_{AEL}. It is important to note that most of the bio-adhesive alternatives that are below the R_{ES} limit are also below that of synthetic resins, making them potential options. In general, the largest number of bio-adhesives that meet the R_{ES} in these PBs are those formulated from soybean, although, given their high involvement on PBs associated with CC,ppm and BBF,P, starch and tannins bio-adhesives are the ones that provide R_{ES} scores closest to the limit value of this parameter, with those formulated from starch having the highest potential to be considered as environmentally sustainable, as the scores obtained are generally lower than the characteristics of biobinders formulated from tannins.

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Table 29.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{GVA}$, at Sweden level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	7.27	2.42	0.22	0.04	2.20	7.32	0.02
OSL-NIPU	2.87	1.21	0.21	0.03	0.98	4.66	0.02
SPI-NIPU	6.79	213.87	0.11	0.04	2.21	7.40	5.41
T-NIPU	8.70	4.83	0.32	0.08	22.94	22.47	0.09
HS-BO	5.52	2.08	1.18	$4.94 \cdot 10^{-3}$	0.46	2.88	71.27
HS-NMA	2.29	57.74	0.03	0.01	0.50	4.86	12.66
OS-Fe	1.16	0.38	0.03	0.10	0.60	2.14	1.90
OS-ECH	7.05	1.29	0.06	0.02	1.08	4.40	6.37
TG	7.02	2.08	1.18	0.01	0.46	2.88	71.27
TH	7.05	2.19	0.11	0.02	1.98	6.01	0.13
TP	6.90	2.19	0.10	0.02	1.90	5.43	0.50
TNA	17.14	12.95	3.61	0.03	1.88	5.76	4.51
TNH	7.12	4.55	1.17	0.03	1.71	5.84	1.55
SF-D	1.06	2.08	1.18	0.01	0.46	2.88	71.27
SF-WP	1.58	2.19	0.11	$1.92 \cdot 10^{-3}$	1.98	6.01	0.13
SF-ER	26.87	2.19	0.10	0.02	1.90	5.43	0.50
SP-EP	3.38	12.95	3.61	0.03	1.88	5.76	4.51
SP-MA	1.53	4.55	1.17	$3.56 \cdot 10^{-3}$	1.71	5.84	1.55
SP-TR	1.74	91.44	0.02	$2.10 \cdot 10^{-3}$	0.47	0.91	98.99
Synthetic	2.36	4.38	0.74	0.03	1.31	7.96	3.24
R_{ES}	1	1	1	1	1	1	1

The scores obtained considering the allocation in Spain (**Table 30**) are higher than those obtained for Sweden, which was expected given the aSOS value obtained for this nation. However, despite this, some analogy can be observed in some scenarios with respect to the R_{ES} values obtained for Sweden. The potential of starch and tannin bio-adhesives for the substitution of synthetic resins is maintained as, although their values exceed the sustainability limit, they are still below those of formaldehyde-based resins. The most notable difference is observed in soy-based bio-adhesives, where proportions exceeding what is considered sustainable by up to 100 points are achieved, thus contributing more significantly to the environmental damage of PBs.

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Table 30.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{GVA}$, at Spanish level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	12.37	4.36	0.38	0.07	3.74	12.45	1.26
OSL-NIPU	4.88	2.16	0.35	0.05	1.67	7.93	1.14
SPI-NIPU	11.55	363.96	0.19	0.07	3.77	12.59	393.49
T-NIPU	14.79	8.36	0.54	0.13	39.00	38.21	6.55
HS-BO	11.58	4.36	2.48	0.01	0.95	6.05	149.51
HS-NMA	4.81	121.13	0.05	0.01	1.05	10.19	26.55
OS-Fe	2.44	0.79	0.06	0.21	1.26	4.49	3.99
OS-ECH	14.79	***2.71***	0.12	0.04	2.27	9.24	13.37
TG	14.73	4.54	0.22	0.03	4.05	11.50	0.21
TH	14.79	4.59	0.23	0.04	4.16	12.60	0.28
TP	14.47	4.59	0.22	0.03	3.99	11.40	1.04
TNA	35.95	27.17	7.57	0.07	3.95	12.08	9.47
TNH	14.94	9.55	2.46	0.05	3.58	12.25	3.26
SF-D	2.22	278.75	0.06	0.02	0.69	1.27	76.97
SF-WP	3.31	169.66	0.05	$4.02 \cdot 10^{-3}$	0.97	1.89	184.98
SF-ER	56.36	449.79	0.14	0.01	1.37	4.36	123.29
SP-EP	7.09	268.12	0.14	0.05	2.37	8.11	289.65
SP-MA	3.21	404.28	0.13	0.01	0.92	2.20	115.64
SP-TR	3.65	191.83	0.05	$4.41 \cdot 10^{-3}$	0.98	1.92	207.67
Synthetic	2.36	4.38	0.74	0.03	1.31	7.96	3.24
R_{ES}	1	1	1	1	1	1	1

7.5.2 Allocation by the combination of egalitarian and utilitarian principle

The Final Consumption Expenditure (FCE) allocation approach has been used as combined egalitarian and utilitarian principle to downscale the planetary boundaries to the continental and regional scales (Bjorn et al., 2020; Walbech and Thesis, 2018), to Europe, Sweden and Spain, respectively.

The reasons for the selection of these territories have been discussed above but are based on its prominence in the timber sector. FCE is an indicator of the expenditures of the community of a territory, including both households and industry, which are used to increase the regional/national economic value where they are consumed and to respond to the individual and collective demands of the citizens. The relationship between FCE and PBs is close, since the consumption pattern and the demands of the population result in the need to produce goods and services, which requires the consumption of resources (fossil and natural) and energy and leads to emissions and waste streams that need to be managed. In this way, it directly affects the BPs and is a source of contribution to them.

To assess the sustainability index of wood-based adhesives analysed, it is first necessary to calculate the allocated safe operating space (aSOS) for the communities of Europe, Sweden and Spain. The allocation considered is based on the evaluation under both industrial and population (POP) scope, $aSOS_{FCE,\ ind+POP}$, To this end, FCE and POP values are taking from available database, being FAO (Food and Agriculture Organization of the United Nations), UNECE (United Nations Economic Commission

for Europe), MITECO (Spanish Ministry for Ecological Transition and Demographic Challenge) (Gobierno de España, n.d.) and World Bank Group- International Development, Poverty & Sustainability.

The data collected for estimate the $aSOS_{FCE}$ is shown in **Table 31**, for both Europe, Sweden and Spain territories. The main difference observed compared to the previous approach considered, where the allocation score for the Spanish region is the lowest within the three territories, is that in this case the lowest allocated values are obtained for Sweden, in the case of $aSOS_{FCE,\ ind+POP}$, and for Europe, when the value chain is considered for allocation, $aSOS_{FCE,\ ind+POP+VC}$.

Table 31. FCE, POP, VC and aSOS values at the European, Sweden and Spanish levels.

FCE_{WS}	$3.71 \cdot 10^{7}$	$9.97 \cdot 10^{8}$	$1.36 \cdot 10^{9}$
$FCE_{R/C}$	$1.13 \cdot 10^{7}$	$3.82 \cdot 10^{5}$	$9.97 \cdot 10^{5}$
$POP_{R/C}$	$7.48 \cdot 10^{8}$	$1.02 \cdot 10^{8}$	$4.67 \cdot 10^{8}$
$VC_{WPP\ R/C}$	$8.96 \cdot 10^{7}$	$6.53 \cdot 10^{5}$	$3.73 \cdot 10^{6}$
VC_{WS}	$9.00 \cdot 10^{8}$	$1.45 \cdot 10^{8}$	$4.17 \cdot 10^{7}$
$aSOS_{FCE,\ ind+POP}$	0.32	3.41	8.24

Once the aSOS score is calculated, it is used to downscale the PBs for the wood adhesives alternatives and to determine the ratio of environmental sustainability, R_{ES}, of the alternative wood adhesives scenarios, which must be less than 1 to consider the scenario as sustainable. For this, the previously obtained LCA values, following the recommendations of the Environmental Footprint report in the selection of the impact calculation methodology, will be divided by the SOS for human activities.

The R_{ES} scores for both bio-adhesives and synthetic resins, considering $aSOS_{FCE,\ ind+POP}$, are shown in **Table 32, 33** and **34**, one per each region. To compare the potential of bio-adhesives with that of resins formulated with formaldehyde, also the scoring values of the synthetic resins in the different PBs have been calculated and are available at the one before the last row of each table. Therefore, those bio-adhesives that have R_{ES} values lower than 1, and as much lower possible, have a lower impact contribution on PBs and could be considered as more sustainable wood adhesive options.

All bio-adhesives analysed here are below the threshold values of the environmental sustainability ratio, using the allocation criteria of $aSOS_{FCE,ind+POP,}$ when considering the allocation approaches to European, Swedish and Spanish regions. This is an indicator of their suitability for wood-based panel production. However, there are some impact categories where a higher contribution is observed, i.e., where the R_{ES} ratios obtained are higher than those of synthetic resins, and therefore this is where efforts and sensitivity analyses to reduce environmental burdens should be focused. The categories where this is the case are those corresponding to climate change, i.e., PB_{CCimb} and PB_{CCppm}, and $PB_{BF,P}$, although for some bio-adhesives, such as T-NIPU, Tannin-DMC and Tannin-HDMA, the planetary limits of formaldehyde-based resins are also exceeded in the PB_{OA} and PB_{AEL} categories.

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Table 32. R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at European level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$2.63 \cdot 10^{-3}$	$9.29 \cdot 10^{-4}$	$8.01 \cdot 10^{-5}$	$5.84 \cdot 10^{-6}$	$1.90 \cdot 10^{-3}$	$2.65 \cdot 10^{-3}$	$2.69 \cdot 10^{-4}$
OSL-NIPU	$1.04 \cdot 10^{-3}$	$4.60 \cdot 10^{-4}$	$7.46 \cdot 10^{-5}$	$2.60 \cdot 10^{-6}$	$1.44 \cdot 10^{-3}$	$1.69 \cdot 10^{-3}$	$2.42 \cdot 10^{-4}$
SPI-NIPU	$2.46 \cdot 10^{-3}$	$7.75 \cdot 10^{-2}$	$4.04 \cdot 10^{-5}$	$5.88 \cdot 10^{-6}$	$2.02 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$	$8.38 \cdot 10^{-2}$
T-NIPU	$3.15 \cdot 10^{-3}$	$1.78 \cdot 10^{-3}$	$1.14 \cdot 10^{-4}$	$6.09 \cdot 10^{-5}$	$3.87 \cdot 10^{-3}$	$8.13 \cdot 10^{-3}$	$1.39 \cdot 10^{-3}$
HS-BO	$2.47 \cdot 10^{-3}$	$2.73 \cdot 10^{-2}$	$5.28 \cdot 10^{-4}$	$1.49 \cdot 10^{-6}$	$3.01 \cdot 10^{-3}$	$1.29 \cdot 10^{-3}$	$3.18 \cdot 10^{-2}$
HS-NMA	$1.02 \cdot 10^{-3}$	$2.58 \cdot 10^{-2}$	$1.14 \cdot 10^{-5}$	$1.64 \cdot 10^{-6}$	3.18·104	$2.17 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$
OS-Fe	$5.20 \cdot 10^{-4}$	$1.69 \cdot 10^{-4}$	$1.21 \cdot 10^{-5}$	$1.96 \cdot 10^{-6}$	$6.10 \cdot 10^{-3}$	$9.56 \cdot 10^{-4}$	$8.49 \cdot 10^{-4}$
OS-ECH	$1.02 \cdot 10^{-3}$	$5.77 \cdot 10^{-4}$	$2.64 \cdot 10^{-5}$	$3.55 \cdot 10^{-6}$	$1.12 \cdot 10^{-3}$	$1.97 \cdot 10^{-3}$	2.85·103
TG	$3.14 \cdot 10^{-3}$	$9.66 \cdot 10^{-4}$	$4.77 \cdot 10^{-5}$	$6.32 \cdot 10^{-6}$	$8.88 \cdot 10^{-4}$	$2.45 \cdot 10^{-3}$	$4.47 \cdot 10^{-5}$
TH	$3.15 \cdot 10^{-3}$	$9.77 \cdot 10^{-4}$	$4.86 \cdot 10^{-5}$	$6.49 \cdot 10^{-6}$	$1.15 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$	$5.95 \cdot 10^{-5}$
TP	$3.08 \cdot 10^{-3}$	$9.48 \cdot 10^{-4}$	$4.63 \cdot 10^{-5}$	$6.24 \cdot 10^{-6}$	$9.28 \cdot 10^{-3}$	$2.43 \cdot 10^{-3}$	$2.22 \cdot 10^{-4}$
TNA	$7.65 \cdot 10^{-3}$	$5.78 \cdot 10^{-3}$	$1.61 \cdot 10^{-3}$	$6.17 \cdot 10^{-6}$	$2.01 \cdot 10^{-3}$	$2.57 \cdot 10^{-3}$	$2.02 \cdot 10^{-3}$
TNH	$3.18 \cdot 10^{-3}$	$2.03 \cdot 10^{-3}$	$5.23 \cdot 10^{-4}$	$5.59 \cdot 10^{-6}$	$1.53 \cdot 10^{-3}$	$2.61 \cdot 10^{-3}$	$6.93 \cdot 10^{-4}$
SF-D	$4.72 \cdot 10^{-4}$	$5.93 \cdot 10^{-2}$	$1.23 \cdot 10^{-5}$	$1.08 \cdot 10^{-6}$	$6.13 \cdot 10^{-4}$	$2.71 \cdot 10^{-4}$	$1.64 \cdot 10^{-2}$
SF-WP	$7.06 \cdot 10^{-4}$	$3.61 \cdot 10^{-2}$	$1.13 \cdot 10^{-5}$	$1.52 \cdot 10^{-6}$	$1.17 \cdot 10^{-4}$	$4.02 \cdot 10^{-4}$	$3.94 \cdot 10^{-2}$
SF-ER	$1.20 \cdot 10^{-2}$	$9.58 \cdot 10^{-2}$	$3.01 \cdot 10^{-5}$	$2.14 \cdot 10^{-6}$	$3.21 \cdot 10^{-4}$	$9.27 \cdot 10^{-4}$	$2.63 \cdot 10^{-2}$
SP-EP	$1.51 \cdot 10^{-3}$	$5.71 \cdot 10^{-2}$	$3.03 \cdot 10^{-5}$	$3.70 \cdot 10^{-6}$	$1.46 \cdot 10^{-3}$	$1.73 \cdot 10^{-3}$	$6.17 \cdot 10^{-2}$
SP-MA	$6.83 \cdot 10^{-4}$	$8.61 \cdot 10^{-2}$	$2.74 \cdot 10^{-5}$	$1.44 \cdot 10^{-6}$	$2.17 \cdot 10^{-4}$	$4.68 \cdot 10^{-4}$	$2.46 \cdot 10^{-2}$
SP-TR	$7.78 \cdot 10^{-4}$	$4.08 \cdot 10^{-2}$	$1.11 \cdot 10^{-5}$	$1.53 \cdot 10^{-6}$	$1.28 \cdot 10^{-4}$	$4.08 \cdot 10^{-4}$	$4.42 \cdot 10^{-2}$
Synthetic	$1.06 \cdot 10^{-3}$	$1.96 \cdot 10^{-3}$	$3.28 \cdot 10^{-4}$	$4.30 \cdot 10^{-6}$	$1.57 \cdot 10^{-3}$	$1.45 \cdot 10^{-1}$	$1.45 \cdot 10^{-3}$
R_{ES}	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Soy-based bio-adhesives show the highest exceedances of the limits set for synthetic resins in the PB_{CCppm} and $PB_{BF,P}$ categories, where all of them have reached higher values and, therefore, show a lower degree of environmental sustainability. In a previous report (Arias et al., 2020), it was concluded that the use of some chemicals as crosslinking agents, such as dicyandiamide or hexamethylene diamine, are one of the causes of such a high impact (Arias et al., 2021b). This is why a reduction in the dosage of these chemicals, as well as the option of modifying the crosslinking agent used in the formulation of the bio-adhesive, were considered as viable and appropriate alternatives in the search for impact reduction. Regarding the use of soy protein, SPI, it is worth mentioning that its extraction process is characterized by high energy consumption, which will imply a high environmental contribution, a fact that is observable for all the regions under assessment, where the SPI-NIPU bio-adhesive exceeds the limit values of the synthetic resins in the previously mentioned categories, and it is also worth mentioning that it is very close to the limit values in all the PBs, with the exception of PPB N-flow where this bio-adhesive is surpassed by T-NIPU. On the other hand, analysing the different bio-adhesive scenarios at the global level, it can be considered that tannin-based bio-adhesives seem to be the most environmentally sustainable alternative, as all scenarios are below the limits of formaldehyde-based resins, with the only exception of a slightly higher value in the PB_{CC} and PB_{OA} categories, but lower than that of the others bio-adhesive scenarios.

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Contrary to what happened in the case of the use of GVA as an indicator of a country's economic prosperity, where the enlargement of Europe to the national level (**Tables 33** and **34**) implied a decrease in GVA and thus a "negative" impact on the environmental sustainability ratio, as it is inversely proportional to the allocated safe operating space (aSOS). This fact resulted in an increase in the value of R_{ES}, leading to a ratio above 1, indicating the lack of sustainability of the analysed bio-adhesive scenario. But in the case of the FCE, a downscaling to national regions results in a higher aSOS value, which has a "positive" impact on the sustainability score, as it contributes more to a lower R_{ES} value. However, it is important to mention the point that, despite the lower aSOS value for the European continent, environmental sustainability is also achieved for all studied bio-adhesive scenarios. However, it is important to note that not all bio-adhesive scenarios have lower R_{ES} values than those characteristic for synthetic resins. This fact of exceeding the limit for formaldehyde-based resins but remaining below the RES limit mainly affects the categories associated with phosphorus cycling cycle, $PB_{BF,P}$ and climate change, i.e., $PB_{CC,imb}$, $PB_{CC,ppm}$ and, in the case of some tannin bio-adhesives scenarios, also the PB_{OA} category.

Table 33.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at Sweden level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$2.45\cdot10^{-4}$	$8.64\cdot10^{-5}$	$7.45\cdot10^{-6}$	$5.43\cdot10^{-7}$	$1.77\cdot10^{-4}$	$2.46\cdot10^{-4}$	$2.50\cdot10^{-5}$
OSL-NIPU	$9.66\cdot10^{-5}$	$4.27\cdot10^{-5}$	$6.93\cdot10^{-6}$	$2.42\cdot10^{-7}$	$1.34\cdot10^{-4}$	$1.57\cdot10^{-4}$	$2.25\cdot10^{-5}$
SPI-NIPU	$2.29\cdot10^{-4}$	$7.21\cdot10^{-3}$	$3.76\cdot10^{-6}$	$5.47\cdot10^{-7}$	$1.88\cdot10^{-4}$	$2.49\cdot10^{-4}$	$7.79\cdot10^{-3}$
T-NIPU	$2.93\cdot10^{-4}$	$1.66\cdot10^{-4}$	$1.06\cdot10^{-5}$	$5.66\cdot10^{-6}$	$3.59\cdot10^{-4}$	$7.56\cdot10^{-4}$	$1.30\cdot10^{-4}$
HS-BO	$2.29\cdot10^{-4}$	$2.54\cdot10^{-3}$	$4.91\cdot10^{-5}$	$1.39\cdot10^{-7}$	$2.80\cdot10^{-5}$	$1.20\cdot10^{-4}$	$2.96\cdot10^{-3}$
HS-NMA	$9.52\cdot10^{-5}$	$2.40\cdot10^{-3}$	$1.06\cdot10^{-6}$	$1.52\cdot10^{-7}$	$2.96\cdot10^{-5}$	$2.02\cdot10^{-4}$	$5.26\cdot10^{-4}$
OS-Fe	$4.83\cdot10^{-5}$	$1.57\cdot10^{-5}$	$1.13\cdot10^{-6}$	$1.82\cdot10^{-7}$	$5.67\cdot10^{-4}$	$8.89\cdot10^{-5}$	$7.90\cdot10^{-5}$
OS-ECH	$9.49\cdot10^{-5}$	$5.37\cdot10^{-5}$	$2.45\cdot10^{-6}$	$3.30\cdot10^{-7}$	$1.04\cdot10^{-4}$	$1.83\cdot10^{-4}$	$2.65\cdot10^{-4}$
TG	$2.92\cdot10^{-4}$	$8.98\cdot10^{-5}$	$4.44\cdot10^{-6}$	$5.88\cdot10^{-7}$	$8.25\cdot10^{-5}$	$2.28\cdot10^{-4}$	$4.16\cdot10^{-6}$
TH	$2.93\cdot10^{-4}$	$9.09\cdot10^{-5}$	$4.52\cdot10^{-6}$	$6.03\cdot10^{-7}$	$1.07\cdot10^{-4}$	$2.50\cdot10^{-4}$	$5.53\cdot10^{-6}$
TP	$2.86\cdot10^{-4}$	$8.81\cdot10^{-5}$	$4.31\cdot10^{-6}$	$5.80\cdot10^{-7}$	$8.63\cdot10^{-5}$	$2.26\cdot10^{-4}$	$2.06\cdot10^{-5}$
TNA	$7.12\cdot10^{-4}$	$5.38\cdot10^{-4}$	$1.50\cdot10^{-4}$	$5.74\cdot10^{-7}$	$1.87\cdot10^{-4}$	$2.39\cdot10^{-4}$	$1.87\cdot10^{-4}$
TNH	$2.96\cdot10^{-4}$	$1.89\cdot10^{-4}$	$4.87\cdot10^{-5}$	$5.19\cdot10^{-7}$	$1.43\cdot10^{-4}$	$2.42\cdot10^{-4}$	$6.45\cdot10^{-5}$
SF-D	$4.39\cdot10^{-5}$	$5.52\cdot10^{-3}$	$1.15\cdot10^{-6}$	$1.01\cdot10^{-7}$	$5.70\cdot10^{-5}$	$2.52\cdot10^{-5}$	$1.52\cdot10^{-3}$
SF-WP	$6.56\cdot10^{-5}$	$3.36\cdot10^{-3}$	$1.05\cdot10^{-6}$	$1.41\cdot10^{-7}$	$1.09\cdot10^{-5}$	$3.74\cdot10^{-5}$	$3.66\cdot10^{-3}$
SF-ER	$1.12\cdot10^{-3}$	$8.90\cdot10^{-3}$	$2.80\cdot10^{-6}$	$1.99\cdot10^{-7}$	$2.98\cdot10^{-5}$	$8.62\cdot10^{-5}$	$2.44\cdot10^{-3}$
SP-EP	$1.40\cdot10^{-4}$	$5.31\cdot10^{-3}$	$2.82\cdot10^{-6}$	$3.44\cdot10^{-7}$	$1.36\cdot10^{-4}$	$1.61\cdot10^{-4}$	$5.73\cdot10^{-3}$
SP-MA	$6.36\cdot10^{-5}$	$8.00\cdot10^{-3}$	$2.55\cdot10^{-6}$	$1.34\cdot10^{-7}$	$2.02\cdot10^{-5}$	$4.35\cdot10^{-5}$	$2.29\cdot10^{-3}$
SP-TR	$7.23\cdot10^{-5}$	$3.80\cdot10^{-3}$	$1.03\cdot10^{-6}$	$1.43\cdot10^{-7}$	$1.19\cdot10^{-5}$	$3.80\cdot10^{-5}$	$4.11\cdot10^{-3}$
Synthetic	$9.81\cdot10^{-5}$	$1.82\cdot10^{-4}$	$3.05\cdot10^{-5}$	$4.00\cdot10^{-7}$	$1.46\cdot10^{-4}$	$1.35\cdot10^{-2}$	$1.35\cdot10^{-4}$
R_{ES}	1	1	1	1	1	1	1

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Table 34.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at Spanish level. Table codes: green and bold bio-adhesive acronym (bio-adhesive alternative meeting the threshold in all PBs categories), italics and bold score (bio-adhesive R_{ES} score lower than synthetic score), orange shadow (unsustainable scenario for the PBs category) and green shadow (sustainable scenario for all PBs categories).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$1.01\cdot10^{-4}$	$3.58\cdot10^{-5}$	$3.09\cdot10^{-6}$	$2.25\cdot10^{-7}$	$7.32\cdot10^{-5}$	$1.02\cdot10^{-4}$	$1.04\cdot10^{-5}$
OSL-NIPU	$4.00\cdot10^{-5}$	$1.77\cdot10^{-5}$	$2.87\cdot10^{-6}$	$1.00\cdot10^{-7}$	$5.56\cdot10^{-5}$	$6.50\cdot10^{-5}$	$9.33\cdot10^{-6}$
SPI-NIPU	$9.48\cdot10^{-5}$	$2.99\cdot10^{-3}$	$1.56\cdot10^{-6}$	$2.27\cdot10^{-7}$	$7.78\cdot10^{-5}$	$1.03\cdot10^{-4}$	$3.23\cdot10^{-3}$
T-NIPU	$1.21\cdot10^{-4}$	$6.86\cdot10^{-5}$	$4.41\cdot10^{-6}$	$2.35\cdot10^{-6}$	$1.49\cdot10^{-4}$	$3.13\cdot10^{-4}$	$5.37\cdot10^{-5}$
HS-BO	$9.50\cdot10^{-5}$	$1.05\cdot10^{-3}$	$2.03\cdot10^{-5}$	$5.74\cdot10^{-8}$	$1.16\cdot10^{-5}$	$4.96\cdot10^{-5}$	$1.23\cdot10^{-3}$
HS-NMA	$3.94\cdot10^{-5}$	$9.94\cdot10^{-4}$	$4.39\cdot10^{-7}$	$6.31\cdot10^{-8}$	$1.22\cdot10^{-5}$	$8.36\cdot10^{-5}$	$2.18\cdot10^{-4}$
OS-Fe	$2.00\cdot10^{-5}$	$6.51\cdot10^{-6}$	$4.68\cdot10^{-7}$	$7.56\cdot10^{-8}$	$2.35\cdot10^{-4}$	$3.68\cdot10^{-5}$	$3.27\cdot10^{-5}$
OS-ECH	$3.93\cdot10^{-5}$	$2.22\cdot10^{-5}$	$1.02\cdot10^{-6}$	$1.37\cdot10^{-7}$	$4.32\cdot10^{-5}$	$7.58\cdot10^{-5}$	$1.10\cdot10^{-4}$
TG	$1.21\cdot10^{-4}$	$3.72\cdot10^{-5}$	$1.84\cdot10^{-6}$	$2.43\cdot10^{-7}$	$3.42\cdot10^{-5}$	$9.43\cdot10^{-5}$	$1.72\cdot10^{-6}$
TH	$1.21\cdot10^{-4}$	$3.76\cdot10^{-5}$	$1.87\cdot10^{-6}$	$2.50\cdot10^{-7}$	$4.43\cdot10^{-5}$	$1.03\cdot10^{-4}$	$2.29\cdot10^{-6}$
TP	$1.19\cdot10^{-4}$	$3.65\cdot10^{-5}$	$1.78\cdot10^{-6}$	$2.40\cdot10^{-7}$	$3.57\cdot10^{-5}$	$9.35\cdot10^{-5}$	$8.54\cdot10^{-6}$
TNA	$2.95\cdot10^{-4}$	$2.23\cdot10^{-4}$	$6.21\cdot10^{-5}$	$2.38\cdot10^{-7}$	$7.75\cdot10^{-5}$	$9.90\cdot10^{-5}$	$7.77\cdot10^{-5}$
TNH	$1.23\cdot10^{-4}$	$7.83\cdot10^{-5}$	$2.02\cdot10^{-5}$	$2.15\cdot10^{-7}$	$5.91\cdot10^{-5}$	$1.00\cdot10^{-4}$	$2.67\cdot10^{-5}$
SF-D	$1.82\cdot10^{-5}$	$2.29\cdot10^{-3}$	$4.75\cdot10^{-7}$	$4.17\cdot10^{-8}$	$2.36\cdot10^{-5}$	$1.04\cdot10^{-5}$	$6.31\cdot10^{-4}$
SF-WP	$2.72\cdot10^{-5}$	$1.39\cdot10^{-3}$	$4.34\cdot10^{-7}$	$5.86\cdot10^{-8}$	$4.50\cdot10^{-6}$	$1.55\cdot10^{-5}$	$1.52\cdot10^{-3}$
SF-ER	$4.62\cdot10^{-4}$	$3.69\cdot10^{-3}$	$1.16\cdot10^{-6}$	$8.25\cdot10^{-8}$	$1.24\cdot10^{-5}$	$3.57\cdot10^{-5}$	$1.01\cdot10^{-3}$
SP-EP	$5.81\cdot10^{-5}$	$2.20\cdot10^{-3}$	$1.17\cdot10^{-6}$	$1.42\cdot10^{-7}$	$5.64\cdot10^{-5}$	$6.66\cdot10^{-5}$	$2.38\cdot10^{-3}$
SP-MA	$2.63\cdot10^{-5}$	$3.32\cdot10^{-3}$	$1.06\cdot10^{-6}$	$5.56\cdot10^{-8}$	$8.35\cdot10^{-6}$	$1.80\cdot10^{-5}$	$9.49\cdot10^{-4}$
SP-TR	$3.00\cdot10^{-5}$	$1.57\cdot10^{-3}$	$4.26\cdot10^{-7}$	$5.91\cdot10^{-8}$	$4.93\cdot10^{-6}$	$1.57\cdot10^{-5}$	$1.70\cdot10^{-3}$
Synthetic	$4.06\cdot10^{-5}$	$7.54\cdot10^{-5}$	$1.27\cdot10^{-5}$	$1.66\cdot10^{-7}$	$6.06\cdot10^{-5}$	$5.57\cdot10^{-3}$	$5.58\cdot10^{-5}$
R_{ES}	1.00	1.00	1.00	1.00	1.00	1.00	1.00

7.5.3 Allocation by grandfathering principle

In this case, for developing the allocation, three main values are needed, the ones previously required for the combined egalitarian and utilitarian principle, namely the population (POP) and the gross value added (GVA), with the addition of the value chain (VC), in which the related GHG emissions of the wood sector, per country and European level, should be also assessed. In this regard, the using this allocation procedure, the three pillars of sustainability are globally assessed, the environmental with the VC score, the social with the POP value and the economic with the GVA.

Bearing this in mind, a new aSOS is obtained, known as the $aSOS_{FCE,ind+POP+VC}$ calculated by evaluating the data available on **Table 35** for the European, Sweden and Spanish regions.

Table 35. FCE, POP, VC and aSOS values at the European, Sweden and Spanish levels.

FCE_{WS}	$3.71\cdot10^{7}$	$9.97\cdot10^{8}$	$1.36\cdot10^{9}$
$FCE_{R/C}$	$1.13\cdot10^{7}$	$3.82\cdot10^{5}$	$9.97\cdot10^{5}$
$POP_{R/C}$	$7.48\cdot10^{8}$	$1.02\cdot10^{8}$	$4.67\cdot10^{8}$
$VC_{WPP\ R/C}$	$8.96\cdot10^{7}$	$6.53\cdot10^{5}$	$3.73\cdot10^{6}$
VC_{WS}	$9.00\cdot10^{8}$	$1.45\cdot10^{8}$	$4.17\cdot10^{7}$
$aSOS_{FCE,\ ind+POP+VC}$	$3.16\cdot10^{-2}$	$1.54\cdot10^{-2}$	0.74

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According to the data given, the results obtained considering the grandfathering allocation are shown on **Table 36** (European level), **Table 37** (Sweden region) and **Table 38** (Spanish territory).

Table 36. R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at European level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$2.64 \cdot 10^{-2}$	$9.32 \cdot 10^{-3}$	$8.04 \cdot 10^{-4}$	$5.86 \cdot 10^{-5}$	$1.91 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$	$2.70 \cdot 10^{-3}$
OSL-NIPU	$1.04 \cdot 10^{-2}$	$4.61 \cdot 10^{-3}$	$7.49 \cdot 10^{-4}$	$2.61 \cdot 10^{-5}$	$1.45 \cdot 10^{-2}$	$1.69 \cdot 10^{-2}$	$2.43 \cdot 10^{-3}$
SPI-NIPU	$2.47 \cdot 10^{-2}$	$7.78 \cdot 10^{-1}$	$4.06 \cdot 10^{-4}$	$5.90 \cdot 10^{-5}$	$2.03 \cdot 10^{-2}$	$2.69 \cdot 10^{-2}$	$8.41 \cdot 10^{-1}$
T-NIPU	$3.16 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$	$1.15 \cdot 10^{-3}$	$6.11 \cdot 10^{-4}$	$3.88 \cdot 10^{-2}$	$8.17 \cdot 10^{-2}$	$1.40 \cdot 10^{-2}$
HS-BO	$2.48 \cdot 10^{-2}$	$2.74 \cdot 10^{-1}$	$5.30 \cdot 10^{-3}$	$1.50 \cdot 10^{-5}$	$3.02 \cdot 10^{-3}$	$1.29 \cdot 10^{-2}$	$3.20 \cdot 10^{-1}$
HS-NMA	$1.03 \cdot 10^{-2}$	$2.59 \cdot 10^{-1}$	$1.14 \cdot 10^{-4}$	$1.64 \cdot 10^{-5}$	$3.19 \cdot 10^{-3}$	$2.18 \cdot 10^{-2}$	$5.68 \cdot 10^{-2}$
OS-Fe	$5.22 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$	$1.22 \cdot 10^{-4}$	$1.97 \cdot 10^{-5}$	$6.12 \cdot 10^{-2}$	$9.60 \cdot 10^{-3}$	$8.53 \cdot 10^{-3}$
OS-ECH	$1.02 \cdot 10^{-2}$	$5.79 \cdot 10^{-3}$	$2.65 \cdot 10^{-4}$	$3.56 \cdot 10^{-5}$	$1.13 \cdot 10^{-2}$	$1.97 \cdot 10^{-2}$	$2.86 \cdot 10^{-2}$
TG	$3.15 \cdot 10^{-2}$	$9.69 \cdot 10^{-3}$	$4.79 \cdot 10^{-4}$	$6.34 \cdot 10^{-5}$	$8.91 \cdot 10^{-3}$	$2.46 \cdot 10^{-2}$	$4.49 \cdot 10^{-4}$
TH	$3.16 \cdot 10^{-2}$	$9.81 \cdot 10^{-3}$	$4.88 \cdot 10^{-4}$	$6.51 \cdot 10^{-5}$	$1.16 \cdot 10^{-2}$	$2.69 \cdot 10^{-2}$	$5.97 \cdot 10^{-4}$
TP	$3.09 \cdot 10^{-2}$	$9.51 \cdot 10^{-3}$	$4.65 \cdot 10^{-4}$	$6.26 \cdot 10^{-5}$	$9.31 \cdot 10^{-3}$	$2.44 \cdot 10^{-2}$	$2.23 \cdot 10^{-3}$
TNA	$7.68 \cdot 10^{-2}$	$5.81 \cdot 10^{-2}$	$1.62 \cdot 10^{-2}$	$6.20 \cdot 10^{-5}$	$2.02 \cdot 10^{-2}$	$2.58 \cdot 10^{-2}$	$2.02 \cdot 10^{-2}$
TNH	$3.19 \cdot 10^{-2}$	$2.04 \cdot 10^{-2}$	$5.25 \cdot 10^{-3}$	$5.61 \cdot 10^{-5}$	$1.54 \cdot 10^{-2}$	$2.62 \cdot 10^{-2}$	$6.96 \cdot 10^{-3}$
SF-D	$4.74 \cdot 10^{-3}$	$5.96 \cdot 10^{-1}$	$1.24 \cdot 10^{-4}$	$1.09 \cdot 10^{-5}$	$6.15 \cdot 10^{-3}$	$2.72 \cdot 10^{-3}$	$1.65 \cdot 10^{-1}$
SF-WP	$7.08 \cdot 10^{-3}$	$3.63 \cdot 10^{-1}$	$1.13 \cdot 10^{-4}$	$1.53 \cdot 10^{-5}$	$1.17 \cdot 10^{-3}$	$4.03 \cdot 10^{-3}$	$3.95 \cdot 10^{-1}$
SF-ER	$1.20 \cdot 10^{-1}$	$9.61 \cdot 10^{-1}$	$3.02 \cdot 10^{-4}$	$2.15 \cdot 10^{-5}$	$3.22 \cdot 10^{-3}$	$9.31 \cdot 10^{-3}$	$2.63 \cdot 10^{-1}$
SP-EP	$1.51 \cdot 10^{-2}$	$5.73 \cdot 10^{-1}$	$3.04 \cdot 10^{-4}$	$3.71 \cdot 10^{-5}$	$1.47 \cdot 10^{-2}$	$1.73 \cdot 10^{-2}$	$6.19 \cdot 10^{-1}$
SP-MA	$6.86 \cdot 10^{-3}$	$8.64 \cdot 10^{-1}$	$2.75 \cdot 10^{-4}$	$1.45 \cdot 10^{-5}$	$2.18 \cdot 10^{-3}$	$4.69 \cdot 10^{-3}$	$2.47 \cdot 10^{-1}$
SP-TR	$7.81 \cdot 10^{-3}$	$4.10 \cdot 10^{-1}$	$1.11 \cdot 10^{-4}$	$1.54 \cdot 10^{-5}$	$1.28 \cdot 10^{-3}$	$4.10 \cdot 10^{-3}$	$4.44 \cdot 10^{-1}$
Synthetic	$1.06 \cdot 10^{-2}$	$1.96 \cdot 10^{-2}$	$3.30 \cdot 10^{-3}$	$4.32 \cdot 10^{-5}$	$1.58 \cdot 10^{-2}$	1.45·10+00	$1.45 \cdot 10^{-2}$
R_{ES}	1.00	1.00	1.00	1.00	1.00	1.00	1.00

For the R_{ES} scores using $aSOS_{FCE,\ ind+POP+VC}$, a similar trend to that of using $aSOS_{FCE,\ ind+POP}$ could be seen, since for the regional allocation of Spain better results are obtained, as a lower value for R_{ES} is obtained, which implies a huge sustainability potential of the adhesive scenarios under assessment. The reason for this fact is based on the same premise as for the previous case, the value of the allocated safe operating space for Spain is the highest compared to that of Sweden or Europe, which provides a larger margin in the value of the sustainability ratio obtained. However, it is important to bear in mind that the value chain of wood products in the Spanish region is smaller, indicating a lower productive capacity.

Bearing this in mind, it is observed that the most affected PB, that is, where a higher contribution value is obtained and, therefore, a lower degree of sustainability, is that of biogeochemical nitrogen flow. The R_{ES} score obtained is higher than the planetary limit for the case of synthetic resins, but nevertheless remains below the permitted value for all bio-adhesive scenarios. Therefore, it could be concluded that, in this case, the potential of bio-adhesives to be considered as sustainable production models is higher than for synthetic resins. On the other hand, the values obtained for the other BPs are within the

limits established to maintain the natural balance of the earth, apart from the $PB_{CC,ppm}$ category for the case of starch-based bio-adhesives, where some exceeding of the limit is appreciated, although not to a great extent.

Table 37. R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at Sweden level. Table codes: green shadow (bio-adhesive R_{ES} score lower than synthetic score) and green and bold bio-adhesive acronym (bio-adhesive alternative sustainable).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$5.44 \cdot 10^{-2}$	$1.92 \cdot 10^{-2}$	$1.66 \cdot 10^{-3}$	$1.21 \cdot 10^{-4}$	$3.93 \cdot 10^{-2}$	$5.48 \cdot 10^{-2}$	$5.55 \cdot 10^{-3}$
OSL-NIPU	$2.15 \cdot 10^{-2}$	$9.50 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$5.38 \cdot 10^{-5}$	$2.98 \cdot 10^{-2}$	$3.49 \cdot 10^{-2}$	$5.01 \cdot 10^{-3}$
SPI-NIPU	$5.08 \cdot 10^{-2}$	1.60·10+00	$8.36 \cdot 10^{-4}$	$1.22 \cdot 10^{-4}$	$4.17 \cdot 10^{-2}$	$5.54 \cdot 10^{-2}$	1.73
T-NIPU	$6.51 \cdot 10^{-2}$	$3.68 \cdot 10^{-2}$	$2.36 \cdot 10^{-3}$	$1.26 \cdot 10^{-3}$	$7.99 \cdot 10^{-2}$	$1.68 \cdot 10^{-1}$	$2.88 \cdot 10^{-2}$
HS-BO	$5.10 \cdot 10^{-2}$	$5.65 \cdot 10^{-1}$	$1.09 \cdot 10^{-2}$	$3.08 \cdot 10^{-5}$	$6.21 \cdot 10^{-3}$	$2.66 \cdot 10^{-2}$	$6.58 \cdot 10^{-1}$
HS-NMA	$2.12 \cdot 10^{-2}$	$5.33 \cdot 10^{-1}$	$2.36 \cdot 10^{-4}$	$3.39 \cdot 10^{-5}$	$6.57 \cdot 10^{-3}$	$4.48 \cdot 10^{-2}$	$1.17 \cdot 10^{-1}$
OS-Fe	$1.07 \cdot 10^{-2}$	$3.49 \cdot 10^{-3}$	$2.51 \cdot 10^{-4}$	$4.05 \cdot 10^{-5}$	$1.26 \cdot 10^{-1}$	$1.98 \cdot 10^{-2}$	$1.76 \cdot 10^{-2}$
OS-ECH	$2.11 \cdot 10^{-2}$	$1.19 \cdot 10^{-2}$	$5.46 \cdot 10^{-4}$	$7.34 \cdot 10^{-5}$	$2.32 \cdot 10^{-2}$	$4.06 \cdot 10^{-2}$	$5.88 \cdot 10^{-2}$
TG	$6.48 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	$9.86 \cdot 10^{-4}$	$1.31 \cdot 10^{-4}$	$1.83 \cdot 10^{-2}$	$5.06 \cdot 10^{-2}$	$9.24 \cdot 10^{-4}$
TH	$6.51 \cdot 10^{-2}$	$2.02 \cdot 10^{-2}$	$1.01 \cdot 10^{-3}$	$1.34 \cdot 10^{-4}$	$2.38 \cdot 10^{-2}$	$5.55 \cdot 10^{-2}$	$1.23 \cdot 10^{-3}$
TP	$6.37 \cdot 10^{-2}$	$1.96 \cdot 10^{-2}$	$9.57 \cdot 10^{-4}$	$1.29 \cdot 10^{-4}$	$1.92 \cdot 10^{-2}$	$5.02 \cdot 10^{-2}$	$4.58 \cdot 10^{-3}$
TNA	$1.58 \cdot 10^{-1}$	$1.20 \cdot 10^{-1}$	$3.33 \cdot 10^{-2}$	$1.28 \cdot 10^{-4}$	$4.16 \cdot 10^{-2}$	$5.31 \cdot 10^{-2}$	$4.17 \cdot 10^{-2}$
TNH	$6.58 \cdot 10^{-2}$	$4.20 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	$1.15 \cdot 10^{-4}$	$3.17 \cdot 10^{-2}$	$5.39 \cdot 10^{-2}$	$1.43 \cdot 10^{-2}$
SF-D	$9.77 \cdot 10^{-3}$	1.23	$2.55 \cdot 10^{-4}$	$2.24 \cdot 10^{-5}$	$1.27 \cdot 10^{-2}$	$5.60 \cdot 10^{-3}$	$3.39 \cdot 10^{-1}$
SF-WP	$1.46 \cdot 10^{-2}$	$7.47 \cdot 10^{-1}$	$2.33 \cdot 10^{-4}$	$3.14 \cdot 10^{-5}$	$2.41 \cdot 10^{-3}$	$8.31 \cdot 10^{-3}$	$8.14 \cdot 10^{-1}$
SF-ER	$2.48 \cdot 10^{-1}$	1.98	$6.21 \cdot 10^{-4}$	$4.43 \cdot 10^{-5}$	$6.63 \cdot 10^{-3}$	$1.92 \cdot 10^{-2}$	$5.43 \cdot 10^{-1}$
SP-EP	$3.12 \cdot 10^{-2}$	1.18	$6.26 \cdot 10^{-4}$	$7.64 \cdot 10^{-5}$	$3.02 \cdot 10^{-2}$	$3.57 \cdot 10^{-2}$	1.27
SP-MA	$1.41 \cdot 10^{-2}$	1.78	$5.67 \cdot 10^{-4}$	$2.98 \cdot 10^{-5}$	$4.48 \cdot 10^{-3}$	$9.67 \cdot 10^{-3}$	$5.09 \cdot 10^{-1}$
SP-TR	$1.61 \cdot 10^{-2}$	$8.44 \cdot 10^{-1}$	$2.29 \cdot 10^{-4}$	$3.17 \cdot 10^{-5}$	$2.65 \cdot 10^{-3}$	$8.44 \cdot 10^{-3}$	$9.14 \cdot 10^{-1}$
Synthetic	$2.18 \cdot 10^{-2}$	$4.04 \cdot 10^{-2}$	$6.79 \cdot 10^{-3}$	$8.90 \cdot 10^{-5}$	$3.25 \cdot 10^{-2}$	2.99	$2.99 \cdot 10^{-2}$
R_{ES}	1	1	1	1	1	1	1

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Table 38.R_{ES} scores for both bio-adhesives and synthetic resins obtained, considering $aSOS_{FCE,ind+POP}$, at Spanish level. Table codes: green and bold bio-adhesive acronym (bio-adhesive alternative meeting the threshold in all PBs categories), italics and bold score (bio-adhesive R_{ES} score lower than synthetic score), orange shadow (unsustainable scenario for the PBs category) and green shadow (sustainable scenario for all PBs categories).

	CC imb	CC ppm	OA	SOD	AEL	BBF, N	BBF, P
KL-NIPU	$1.14 \cdot 10^{-3}$	$4.01 \cdot 10^{-4}$	$3.46 \cdot 10^{-5}$	$3.44 \cdot 10^{-4}$	$6.02 \cdot 10^{-6}$	$1.14 \cdot 10^{-3}$	$1.16 \cdot 10^{-4}$
OSL-NIPU	$4.49 \cdot 10^{-4}$	$1.98 \cdot 10^{-4}$	$3.22 \cdot 10^{-5}$	$1.53 \cdot 10^{-4}$	$4.57 \cdot 10^{-6}$	$7.28 \cdot 10^{-4}$	$1.05 \cdot 10^{-4}$
SPI-NIPU	$1.06 \cdot 10^{-3}$	$3.34 \cdot 10^{-2}$	$1.75 \cdot 10^{-5}$	$3.46 \cdot 10^{-4}$	$6.39 \cdot 10^{-6}$	$1.16 \cdot 10^{-3}$	$3.62 \cdot 10^{-2}$
T-NIPU	$1.36 \cdot 10^{-3}$	$7.68 \cdot 10^{-4}$	$4.94 \cdot 10^{-5}$	$3.58 \cdot 10^{-3}$	$1.22 \cdot 10^{-5}$	$3.51 \cdot 10^{-3}$	$6.02 \cdot 10^{-4}$
HS-BO	$1.06 \cdot 10^{-3}$	$1.18 \cdot 10^{-2}$	$2.28 \cdot 10^{-4}$	$8.77 \cdot 10^{-5}$	$9.51 \cdot 10^{-7}$	$5.56 \cdot 10^{-4}$	$1.37 \cdot 10^{-2}$
HS-NMA	$4.42 \cdot 10^{-4}$	$1.11 \cdot 10^{-2}$	$4.92 \cdot 10^{-6}$	$9.64 \cdot 10^{-5}$	$1.01 \cdot 10^{-6}$	$9.36 \cdot 10^{-4}$	$2.44 \cdot 10^{-3}$
OS-Fe	$2.24 \cdot 10^{-4}$	$7.29 \cdot 10^{-5}$	$5.24 \cdot 10^{-6}$	$1.15 \cdot 10^{-4}$	$1.93 \cdot 10^{-5}$	$4.13 \cdot 10^{-4}$	$3.67 \cdot 10^{-4}$
OS-ECH	$4.40 \cdot 10^{-4}$	$2.49 \cdot 10^{-4}$	$1.14 \cdot 10^{-5}$	$2.09 \cdot 10^{-4}$	$3.55 \cdot 10^{-6}$	$8.49 \cdot 10^{-4}$	$1.23 \cdot 10^{-3}$
TG	$1.35 \cdot 10^{-3}$	$4.17 \cdot 10^{-4}$	$2.06 \cdot 10^{-5}$	$3.72 \cdot 10^{-4}$	$2.81 \cdot 10^{-6}$	$1.06 \cdot 10^{-3}$	$1.93 \cdot 10^{-5}$
TH	$1.36 \cdot 10^{-3}$	$4.22 \cdot 10^{-4}$	$2.10 \cdot 10^{-5}$	$3.82 \cdot 10^{-4}$	$3.64 \cdot 10^{-6}$	$1.16 \cdot 10^{-3}$	$2.57 \cdot 10^{-5}$
TP	$1.33 \cdot 10^{-3}$	$4.09 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$	$3.67 \cdot 10^{-4}$	$2.94 \cdot 10^{-6}$	$1.05 \cdot 10^{-3}$	$9.57 \cdot 10^{-5}$
TNA	$3.30 \cdot 10^{-3}$	$2.50 \cdot 10^{-3}$	$6.96 \cdot 10^{-4}$	$3.63 \cdot 10^{-4}$	$6.37 \cdot 10^{-6}$	$1.11 \cdot 10^{-3}$	$8.70 \cdot 10^{-4}$
TNH	$1.37 \cdot 10^{-3}$	$8.77 \cdot 10^{-4}$	$2.26 \cdot 10^{-4}$	$3.29 \cdot 10^{-4}$	$4.86 \cdot 10^{-6}$	$1.13 \cdot 10^{-3}$	$2.99 \cdot 10^{-4}$
SF-D	$2.04 \cdot 10^{-4}$	$2.56 \cdot 10^{-2}$	$5.32 \cdot 10^{-6}$	$6.36 \cdot 10^{-5}$	$1.94 \cdot 10^{-6}$	$1.17 \cdot 10^{-4}$	$7.07 \cdot 10^{-3}$
SF-WP	$3.04 \cdot 10^{-4}$	$1.56 \cdot 10^{-2}$	$4.86 \cdot 10^{-6}$	$8.95 \cdot 10^{-5}$	$3.70 \cdot 10^{-7}$	$1.73 \cdot 10^{-4}$	$1.70 \cdot 10^{-2}$
SF-ER	$5.18 \cdot 10^{-3}$	$4.13 \cdot 10^{-2}$	$1.30 \cdot 10^{-5}$	$1.26 \cdot 10^{-4}$	$1.01 \cdot 10^{-6}$	$4.00 \cdot 10^{-4}$	$1.13 \cdot 10^{-2}$
SP-EP	$6.51 \cdot 10^{-4}$	$2.46 \cdot 10^{-2}$	$1.31 \cdot 10^{-5}$	$2.17 \cdot 10^{-4}$	$4.63 \cdot 10^{-6}$	$7.46 \cdot 10^{-4}$	$2.66 \cdot 10^{-2}$
SP-MA	$2.95 \cdot 10^{-4}$	$3.71 \cdot 10^{-2}$	$1.18 \cdot 10^{-5}$	$8.49 \cdot 10^{-5}$	$6.86 \cdot 10^{-7}$	$2.02 \cdot 10^{-4}$	$1.06 \cdot 10^{-2}$
SP-TR	$3.36 \cdot 10^{-4}$	$1.76 \cdot 10^{-2}$	$4.78 \cdot 10^{-6}$	$9.03 \cdot 10^{-5}$	$4.05 \cdot 10^{-7}$	$1.76 \cdot 10^{-4}$	$1.91 \cdot 10^{-2}$
Synthetic	$4.55 \cdot 10^{-4}$	$8.44 \cdot 10^{-4}$	$1.42 \cdot 10^{-4}$	$2.53 \cdot 10^{-4}$	$4.97 \cdot 10^{-6}$	$6.24 \cdot 10^{-2}$	$6.25 \cdot 10^{-4}$
R_{ES}	1.00	1.00	1.00	1.00	1.00	1.00	1.00

7.6 What has been done and what's next

This chapter has developed a methodological procedure to assess the potential of various wood bio-adhesives considering an extension of the LCA results to the scope of PBs. In this sense, it is possible to analyse the sustainability perspective within a global level, considering the thresholds for planetary boundaries necessary to ensure the stability of the Earth system to avoid endangering the habitability of the planet. On the other hand, seeking to provide a wider scope of the PB score obtained, different allocation principles were considered (utilitarian, egalitarian and grandfathering), which has been scaled to different regions: Europe, Sweden and Spain. In this way, it could be assessed whether the allocated share of safe operating space is exceeded in the regional and continental approaches under evaluation.

It has been observed that the bio-adhesive alternatives analysed within this manuscript could be considered as potential substitutes for synthetic resins for wood-based panel manufacturing. In most of the scenarios, the environmental sustainability ratio is lower than that of synthetics, but there are some PBs where great efforts should be made, as higher unsustainability scores were obtained. This is the case for the PBs associated with climate change and is also seen for the category of biogeochemical flows in some bio-adhesive alternatives.

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On the other hand, the sharing principle considered for the assessment has given rise to far-reaching results, while in the case of GVA Spain was the most disadvantaged territory, as it gave rise to sustainability ratios above 1, which is indicative of a production scenario classified as unsustainable, when studied according to the FCE, the opposite occurred, Spain was the region in which the best potential for sustainable development was obtained.

Although it is certainly complex to identify the most suitable renewable-based raw material alternative for the formulation of wood bio-adhesives, given the variability of the sustainability scores obtained for the different principal approaches and territorial scales, it could be roughly concluded that starch is the most suitable raw material. In most cases, its impact values are below those characteristics of synthetic resins, and its damage scores, in general, do not exceed the established planetary boundaries. Although it is important to mention that in the case of the allocation principle considering the GVA as an indicator parameter, some exceedance of the safe limits of the planetary limits is observed for all the adhesives studied. Therefore, it is important to establish a universal standard methodology that establishes which allocation approach is the most appropriate when assessing production processes on a planetary scale. This is what future research should focus on developing for sustainability assessment of bio-based processes across planetary boundaries.

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SECTION IV
Antimicrobials

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SUMMARY

Listeria monocytogenes is a Gram-positive, facultative anaerobic bacteria that causes listeriosis. This disease, which can be transmitted through food, causes serious public health problems, especially in at-risk populations. Although chemical preservatives and heat treatments can be used to preserve the quality of food products, these treatments affect their nutritional and organoleptic properties. An alternative is the use of antimicrobials, such as nisin, to ensure food safety and avoid the consequences of eventual negligence in the hygienic-sanitary handling of the final product. Traditionally, nisin is produced by microbial fermentation in the exponential growth phase of *Lactococcus lactis*. Due to high cost of this biomolecule, it is important to promote the commercial production of nisin, using cheaper cultivation substrates.

Chapter 8 addresses the technical feasibility and environmental impacts of biotechnological production of nisin (with the co-production of lactic acid) from three food-associated industrial waste streams (cheese whey, sugar beet pulp, and corn stover). To carry out the conceptual design of a process at an early stage of development it is necessary to apply a process simulation tool, SuperPro Designer®, in order to estimate the operating data, inputs, process outputs and foreseen emissions. In this way, the technical feasibility and readiness level of the biotechnological nisin production can be explored. **Chapter 9** follows the same approach as **Chapter 8**, with the difference on the feedstocks used, being in this case two lignocellulosic-based residues: olive pruning and eucalyptus residues.

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8

Biotechnological production of nisin from agro-industrial waste

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SUMMARY

Consumers now have access to almost unlimited sources of information, which leads to a more conscious and demanding consumer profile, interested not only in the quality and characteristics of the product, but also in information on how the product was produced, its geographic origin and the social and economic aspects associated with the production process. Nowadays the fact that consumers perceive a product as natural is a decisive purchasing incentive. Thus, natural products are often minimally processed foods. It seems that "no artificial ingredients", "no additives" and "healthy" are the three most frequent associations in the consumer's mind with the word "natural".

In this sense, the development of natural products with reduced ultra-processing and limited artificial ingredient content should be considered a quality objective. Considering that natural products must be safe at the preservation stage to avoid the presence of pathogens, the use of natural preservatives is necessary. A promising alternative, recognized as a natural GRAS compound, is nisin, a natural antimicrobial with preservative properties. It is not widely used due to the higher cost associated with its production process, mainly because of the synthetic culture media required for the fermentation process.

In this context, an alternative production scheme has been developed in **Chapter 8**, that evaluates the conceptual design and environmental impacts of the biotechnological production of nisin (co-producing lactic acid) from three waste streams from the agro-industrial sectors: cheese whey, sugar beet pulp and corn stover. The valorization of these waste flows offers a series of benefits, since those residual fractions have an adequate composition in sugars, nitrogen compounds and proteins to be used in the formulation of the culture medium.

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8.1 Nisin: a natural bio-preservative

The consumption of natural products with less industrial processing is an increasingly widespread demand. However, to avoid the presence of pathogens in food, it is necessary to add preservatives, most of which are chemical-based and could pose a health risk. In this context, the use of natural bio-preservatives is a remarkable alternative, among which bacteriocins play an important role, as they are not harmful to human health (Abbasiliasi et al., 2017) and are odorless, tasteless and colorless, so they could be added to food products without altering their main properties (Soltani et al., 2020). The use of bacteriocins as bio-preservatives leads to a reduction in the use of chemical preservatives and heat treatments in the food industry. In this way, foods with better organoleptic and nutritional properties are obtained, which is a great advantage given the growing consumer demand for products with less industrial processing and higher nutritional quality (Sánchez-Martín et al., 2019).

Beyond thermal processes and chemical additives, bacteriocins arise as powerful antimicrobial agents and offer the possibility of preserving foods and, in particular, their organoleptic quality. Bacteriocins are heterogenic antimicrobial peptides released extracellularly by Gram+ and Gram- bacteria and, in some cases, also by *Archaea* (Abbasiliasi et al., 2017; Lopetuso et al., 2019). They can trigger an inhibitory activity in the presence of undesirable microorganisms, including bacteria of the same genus and unrelated pathogens, such as *Clostridium* or *Listeria* (Malvido et al., 2019). Class I bacteriocins (lantibiotics) are small peptides that undergo extensive post-translational modification to produce the active peptide.

Nisin, the most studied bacteriocin, belongs to the class I bacteriocins, which are active against a broad spectrum of pathogenic bacteria. The dose of nisin required to obtain the desired effect depends on several factors, including processing and storage conditions, carbon source, chemicals, bacterial load and product formulation. Due to their possible use as natural preservatives, the bacteriocins produced by lactic acid bacteria have been the focus of intense research in recent years. In particular, Nisin A has been classified as Generally Recognized as Safe (GRAS) by the US Food and Drug Administration (Özel et al., 2018) and recognized by WHO (World Health Organization) for use as preservative in the food industry (Cano-Serna et al., 2015). Nisin stands out not only as a natural bio-preservative (Cano-Serna et al., 2015; Özel et al., 2018) but also in the biomedical and pharmaceutical field. Nisin reduces the undesirable effects of certain antibiotics and is effective in the treatment of infections related to drug-resistant pathogens, gastrointestinal, respiratory, among others (Ellis, 2018; Shin et al., 2016). The use of bacteriocins in nanomaterials has shown an interesting potential for anticancer treatment, reducing the growth of tumor cells (Naskar and Kim, 2021).

However, the economic cost associated with the formulation of the commercial culture medium greatly limits its use in the food industry (Guerra et al., 2007; Özel et al., 2018). Its production process costs are high, up to US$ 770 for only 2.5% of pure nisin in 25 g (Guerra et al., 2007; Özel et al., 2018). With the aim of addressing a more efficient nisin production, it is essential to tackle the coupling of biotechnology and circular economy approach through the concept of biorefineries in which the microbial production of nisin can be accomplished from waste streams. The valorization of agri-food sectors waste products, as cheese whey (CW), sugar beet pulp (SBP) and corn stover (CS) would significantly reduce the costs associated with the process, in addition to providing an innovative model of circular biotechnological production, since residues from agricultural activity are being used to obtain a high value-added product such as nisin as well as lactic acid as a by-product of interest.

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It is important to mention that the available alternatives for the valorization of waste resources in biotechnological processes are developed at laboratory scale (Cheng et al., 2018; Costas Malvido et al., 2017; Guerra and Castro, 2003; Khelissa et al., 2021; Vázquez et al., 2006). In this regard, the technologies and equipment selected for the biorefinery process have been based on bibliographical references and other research articles, going through the stages leading to higher productivity and efficiency. For this purpose, the SuperPro Designer® simulation tool has been used to evaluate the biotechnological scenario on a large scale, in order to assess the potential of the process, as it allows the definition of the process flow diagrams and the design of the equipment, with the identification of the main input and output flows of each process stage. To this end, process modelling in combination with LCA allowed addressing the conceptual design and the environmental assessment of a full-scale nisin production process.

8.2 Process description

The co-production process of nisin and lactic acid is developed through three process sections (**Figure 1**). The first section corresponds to the pretreatment of the agri-food residues, necessary for the release of fermentable sugars, which will be used in the fermentation section, in which nisin and lactic acid are obtained. Finally, for purification and separation, a downstream section is completed, from which it is possible to obtain nisin (with a purity above 95%) and lactic acid which could be further used for the manufacture of PLA bioplastic (alternative scenario assessed in **Chapter 10**), a biomaterial that is in the transition phase between research and industrial production.

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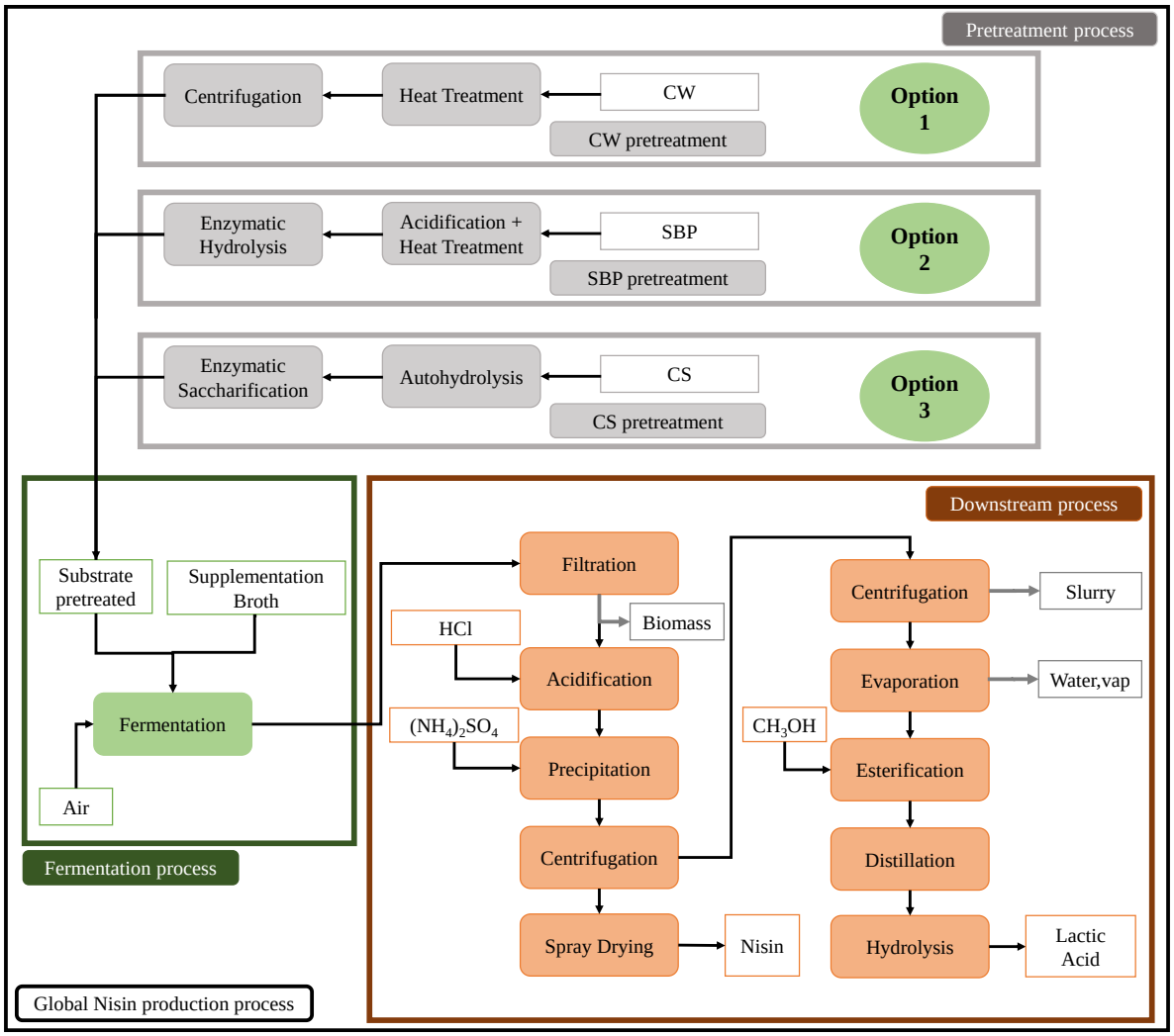

Figure 1. Block diagram of nisin production process with lactic acid recovery using CW (Cheese Whey, Option 1), SBP (Sugar Beet Pulp, Option 2) and CS (Corn Stover, Option 3) as substrates

Considering the fermentation stage and the processing capacity of the downstream process, the amount of nisin produced per batch is estimated at 100 kg. Applying the heuristics of the annual operating time of the facility at 330 days/year, the capacity of each production process is shown in **Table 1**, taking into account that the batch time corresponds to the time required for the total process, considering the three stages, and the cycle time represents the time required for the fermentation stage.

Table 1. Production capacity of the different alternatives studied for nisin production.

Process	CW	SBP	CS
Batch time (h)	77	79	143.58
Cycle time (h)	30.75	25	72
Number of batches per year	256	314	109
Nisin production (kg/year)	25,487.54	31,640.14	10,901.40
Lactic acid production (kg/year)	281,216.73	765,141.76	243,595.91

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8.2.1 Selection of the feedstock: Agri-food residues

When considering a biotechnological process based on the valorization of agricultural and related food sector residues, it is important to examine its availability. Cheese whey (CW), sugar beet pulp (SBP) and corn stover (CS) has been selected as appropriate feedstocks for the production of nisin, given its composition on fermentable sugars. Their availability is high, which converts these waste streams on adequate fractions to be valorized as C-source for the biotechnological processes.

An overview of some quantitative data in the Spanish context report that around 22,251 tons of cheese whey are produced annually (FAOSTAT, 2019), in the case of sugar beet pulp it amounts to 2,752,710 tons (FAOSTAT, 2019) and corn stover is estimated at 4,184,460 tons (FAOSTAT, 2018; Palumbo et al., 2015). These values are indicative of the wide availability of the by-products with an enormous potential for valorization (Forster-Carneiro et al., 2013; Palumbo et al., 2015).

8.2.2 Pretreatment section

The pretreatment section of agri-food waste streams is different for each one of them, since their composition entails the need to adapt the pretreatment according to the type of feedstock used. The rationale behind the pretreatment stage is the release of fermentable sugars to be used later in the fermentation process.

8.2.2.1 Cheese whey

The use of cheese whey requires the simplest pre-treatment among the agri-food residual streams. The main objective of this process is the sterilization of the stream (at 121°C for 15 min) and the precipitation of proteins and fats, followed by a centrifugation (12000xg, 15 min). In this way, the interference of the protein precipitation during the acidification phase of the culture, which is attributed to the formation of lactic acid, is avoided. This allows a more accurate measurement of the amount of biomass formed during the process. The use of CW as carbon substrate source requires the addition of nutrients such as yeast extract, diammonium hydrogen citrate and bacterial peptone, resulting in 23.85 g/L of total sugars, 3.49 g/L of nitrogen and 0.50 g/L of phosphorus (Malvido et al., 2019).

8.2.2.2 Sugar beet pulp

From a technological point of view, the use of sugar beet pulp for fermentation processes is an efficient C-source due to its high cellulose and hemicellulose content and its low lignin content. However, to ensure a higher yield of fermentable sugars, a pre-treatment process combining several stages is necessary: acidification with 2% w/w sulfuric acid, a heat treatment at 121°C, followed by an enzymatic hydrolysis process (Berłowska et al., 2016).

Since the composition of SBP is mainly cellulose and hemicellulose, it is necessary to use enzymes capable of breaking down these polysaccharides into multiple monomers of glucose. Accordingly, cocktails of cellulases and hemicellulases are required, each with a dose of 0.02 mL/g of dry matter (Berłowska et al., 2016). Once the enzymatic hydrolysis is completed, the fermentation medium will be formulated with K_2HPO_4 and NH_4OH.

8.2.2.3 Corn stover

This waste stream requires more severe pre-treatment stages prior to enzymatic hydrolysis. an autohydrolysis step is carried out at 230°C, 150 rpm and a liquid-solid ratio of 9 g water/g corn stover (del Río et al., 2020). As in the previous scenario, an enzymatic process is also required to convert glucan (39.5 g/100 g of corn stover) and hemicelluloses (19.4 g/100 g of corn stover), into their glucose monomer units, to accomplish 70% conversion. The operating conditions used in this process are the following: 48.5°C, 150 rpm and a residence time of 72 h. On the other hand, the consistency of the medium amounts to a value of 4%. Regarding the

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amount of enzymes required at this stage, 25 cellulase FPU (Filter Paper Units)/g substrate and also 5 IU (International Units) of cellobiase are added per FPU of cellulase (del Río et al., 2020). Once the enzymatic hydrolysis is completed, the fermentation medium will be formulated with dipotassium hydrogen phosphate (1 M K_2HPO_4) and ammonium hydroxide (1 M NH_4OH).

8.2.3 Fermentation section

The co-production of nisin and lactic acid corresponds to a microbial fermentation process based on the *Lactococcus lactis* strain (Guerra et al., 2007). The fermentation medium, in addition to the carbon source, in the form of glucose and xylose, requires the addition of nitrogen source as NH_4OH (1 M) and phosphorus as K_2HPO_4 (1 M). The following operating conditions: 30°C, aeration flow rate of 0.5 L/h, 200 rpm and 24 h residence time (Malvido et al., 2019), favor a higher growth of the microbial population and a higher productivity of the process.

The stoichiometry of the process allows to represent the fermentative process of microbial growth and the production of nisin and lactic acid. When CW is used as a source for nisin production, the sugars used by *L. lactis* come from lactose (Equation 1), while the lignocellulosic and agricultural residues provide fermentable sugars (Cheng et al., 2018) (Equation 2).

$$11.85\ \text{Lactose} + 0.81\ NH_4OH + 0.10\ KH_2PO_4 + 10.07\ O_2 + 4.03\ \text{Proteins} \rightarrow 0.82\ \text{Biomass} + 0.29\ \text{Nisin} + 11.18\ CO_2 + 5.23\ \text{Lactic acid} + 9.15\ H_2O \quad \text{Equation 1}$$

$$11.85\ \text{Glucose} + 0.81\ NH_4OH + 0.10\ KH_2PO_4 + 10.07\ O_2 + 4.03\ \text{Proteins} \rightarrow 0.82\ \text{Biomass} + 0.29\ \text{Nisin} + 11.18\ CO_2 + 5.23\ \text{Lactic acid} + 9.15\ H_2O \quad \text{Equation 2}$$

Regarding nutrients, the mass balance considers equivalent amounts of NH_4OH and KH_2PO_4 for the total concentration of nutrients present in the culture medium (Heinzle et al., 2007; Knoll and Buechs, 2007).

Under these conditions, a lactose conversion of 50.83% is guaranteed, leading to biomass and nisin concentrations of 0.82 g/L and 0.49 g/L, respectively. The production of lactic acid as a by-product (5.23 g/L) has to be taken into account, so it was necessary to include additional separation and recovery steps for this compound in the further processing. The glucose conversion value amounts to 91.10%, significantly higher than when using lactose as C source, leading to a fermentation product with concentrations of 0.44 g/L biomass and 0.27 g/L nisin. Regarding the formulation of the culture medium, the use of K_2HPO_4 and NH_4OH has been considered. Once fermentation is complete, the output stream is passed to the downstream section.

8.2.4 Downstream section

This section of the process starts with a vacuum filter, used to separate the biomass, which can be further treated in an anaerobic digestion system (Bijarchiyan et al., 2020; Caposciutti et al., 2020). The valorization of the biogas could be used in the process itself, thus reducing the consumption of fossil resources for the heat requirements.

Once the biomass has been removed, the procedure considered most effective for the recovery and purification of nisin is precipitation with ammonium sulfate: $(NH_4)_2SO_4$ (Tafreshi et al., 2020). This process starts with the acidification of the stream by HCl, and the subsequent precipitation of nisin in the presence of $(NH_4)_2SO_4$. This operation takes place at 4°C for 24 h.

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To separate the precipitated nisin, the output stream from the precipitation equipment is fed into a centrifuge (12000xg, 30 min) and then dried to obtain the final product in solid form with a purity of more than 95%. As the equipment has a filter medium, the nisin is retained and is further washed with water. Accordingly, two streams are obtained, a suspension of nisin and water, and a liquid stream containing lactic acid, which is sent to a recovery sequence. To remove the water content of the nisin suspension, the stream is processed in a fluidized bed dryer. In this way, the nisin can be stored for later use.

As for the recovery of the lactic acid obtained as a fermentation by-product, the process can be divided into three clearly differentiated stages. The first is based on the concentration of the stream after the centrifugation stage to reduce the water content. The second stage involves the esterification reaction of lactic acid with methanol to produce methyl lactate and water, with a conversion of 85% (Gil-Horán et al., 2008). This reaction takes place in a continuous stirred tank reactor (CSTR) at 80°C (using steam as the heating medium).

Methyl lactate is separated in a distillation column at 150°C and 1.013 bar, while the rest of the compounds (i.e., manganese sulphate, ammonium chloride and sulfuric acid) are withdrawn through the bottom of the column and managed as process residues.

As a final step in the lactic acid recovery process, a hydrolysis step is necessary. This is carried out in a CSTR reactor, in which water is added, which will react with the methyl lactate to produce lactic acid and methanol, which can be recycled back to the esterification stage. To develop the separation of methanol and lactic acid, a flash evaporation is performed at 66°C and 1 atm. In this process, 78% w/w of pure lactic acid is obtained, and the methanol is recycled to the CSTR reactor.

8.3 Environmental assessment

The environmental assessment has been conducted in accordance with ISO 14040 guidelines. In this regard, the functional unit (FU) is 1 kg of products, including both nisin and lactic acid. The selection of this FU has been made taking into account the productive capacity of the process, and to facilitate comparison with other reported studies. (Dalgaard et al., 2007; González-García et al., 2013; Muñoz et al., 2014; Nigri et al., 2014; Rumayor et al., 2018).

The scope of the study has been considered within a *cradle-to-gate* approach. In this way, the LCA is developed from the extraction of all the necessary inputs in the process to the production stage. Therefore, transportation activities, the use of the product by the consumer and the processes associated with its recycling, recovery or final disposal are outside the scope of the study.

The Ecoinvent database has been selected for conducting the life-cycle inventories, as it includes basic information on the main inputs, both materials and energy requirements, and outputs, so that it provides valuable information for the quantification of the environmental assessment of the conceptual designs of the processes proposed in this study (Hesketh, 2017). The calculation methodology considered for the development of the LCA has been Recipe 2016 according to Midpoint and EndPoint models.

Considering that the production process is proposed based on process simulation data, transport activities related to the transport of materials or products have not been taken into account, since, when a delocalized process is proposed, there are no fixed transport routes associated with the process.

In relation to specific data for certain chemicals and process inputs and their availability in databases, several simplifications have been assumed. For example, KH_2PO_4 was evaluated as KOH, since the molar ratio of phosphorus in both compounds is the same. For NH_4OH added

as a nitrogen source in the formulation of culture media, NH_4NO_3 was evaluated as an alternative (Ali et al., 2002). Regarding the database considered for the environmental assessment, the Ecoinvent® version 3.2 database was chosen to handle the secondary data associated with the background activities of all utilities (i.e., steam, cooling water), inputs (i.e., whey, SBP, CS, ethanol) and waste streams.

8.3.1 Mass allocation approach

Considering that the production provides two different products: nisin and lactic acid, a mass allocation has been developed in order to analyze which product contributes the most to the environmental profile obtained. The values taken into account for each process scenario are shown in **Table 2**.

Table 2. Mass allocation parameters per product considered for performing allocation procedures.

Scenario	Nisin	Lactic Acid	Nisin	Lactic Acid
	Mass allocation		Economic allocation	
CW	8.31 %	91.69 %	41.19 %	58.81 %
SBP	3.94 %	96.06 %	24.06 %	75.94 %
CS	4.28	95.72	95.73%	95.74%

8.4 Economic Assessment

In the case of the base scenario, the initial investment required for the installation, the income from the sales of the manufactured product and the production costs of each of the elements associated with the industrial facility were determined. As for the initial investment required for the installation, both fixed capital and working capital costs have been considered. This section determines the costs associated with the acquisition of the equipment, including indirect costs, as well as the costs associated with the purchase of the chemicals, such as ethanol, ammonium sulfate or sulfuric acid, and the utilities, i.e., cooling water, steam. As for substrates, as they are considered industrial processing by-product streams, no costs are allocated to their use. In relation to the calculated income and according to the information provided by the Belgian company Handary, the cost of nisin is 85 €/kg.

The economic calculations of the process have assumed a construction period of 9 months and 1 month for the start-up. The average life of the project is assumed to be 30 years with an income tax of 25%. It has been considered that the plant operates at 100% of its production capacity for 11 months a year, leaving 1 month for periodic maintenance. The Net Present Value (NPV) has been selected as the financial indicator that determines the viability of a project, provided that its numerical value is greater than 0 and considering an interest rate of 3%.

8.4.1 Economic allocation approach

From the economic point of view, an allocation procedure has also been developed, based on the same rationale as for mass allocation. The values considered for each process scenario are shown in **Table 2**, in which it could be see that the production of nisin implies higher benefits in the case of sugar beet pulp and corn stover scenarios, while for the cheese whey is still lactic acid the one with the higher percentage of allocation.

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8.5 Environmental results and discussion

In order to evaluate which of the proposed alternatives can be considered the most environmentally friendly, an analysis of the impact results obtained for each manufacturing process has been carried out. In this way, it is possible to identify the critical points of each alternative. First, an overall assessment is made of the impacts associated with the three production processes considered. Once this first analysis has been carried out, the impact values obtained are studied taking into account a mass and an economic allocation, thus making it possible to identify the robustness and variability of the impact results depending on the choice of the allocation procedure and to validate the results independently of the approach considered.

8.5.1 Scenario I. Cheese whey valorization

The summary of the data used for the modelling of Scenario 1 on the valorization of cheese whey is included in **Table 3**. It is included all the inputs and outputs related with the process, obtained by the performance of both mass and energy balances in order to obtain the materials and energy requirements, together with the related emissions and waste flows that are considered as outputs to the technosphere.

Table 3. Main inventory data for the biotechnological valorization of CW residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	117.04	kg	Nisin	8.31	g
Ammonium Sulfate	4.04	kg	Lactic acid	91.69	g
HCl	5.74	kg	*Total*	*1.00*	*kg*
KH_2PO_4	84.34	g			
Methanol	38.29	g	*Emissions to air*		
CW	102.97	kg	Carbon dioxide	1.89	kg
NH_4OH	0.58	kg	Water, vapour	2.12	kg
Water	77.92	kg			
Electricity/heat					
Cooling water	3.18	m^3	*Waste to treatment*		
Steam	383.24	kg	Slurry	17.46	kg
Energy	13.50	kWh	Final waste	2.71	kg

Once the life cycle inventory is completed, the SimaPro software and the ReCiPe MidPoint methodology are used to obtain the environmental profile of the process of cheese whey recovery and valorization. In this regard, **Figure 2** shows the contributions of the different components used for the nisin and lactic acid co-production using cheese whey as substrate. As can be seen, two main contributions can be selected according to the environmental profile: steam (produced from non-renewable energy) and whey as a carbon source for the fermentation process. For the latter, the environmental profile of its production process is attributed to the background activities involved, especially regarding raw materials treatment processing, heat requirements and residual streams treatments (González-García et al., 2013). On the other hand, the use of ammonium sulfate in the production process also implies a certain share in the environmental impacts, especially in the abiotic depletion category due to the significant requirement of energy in the production process.

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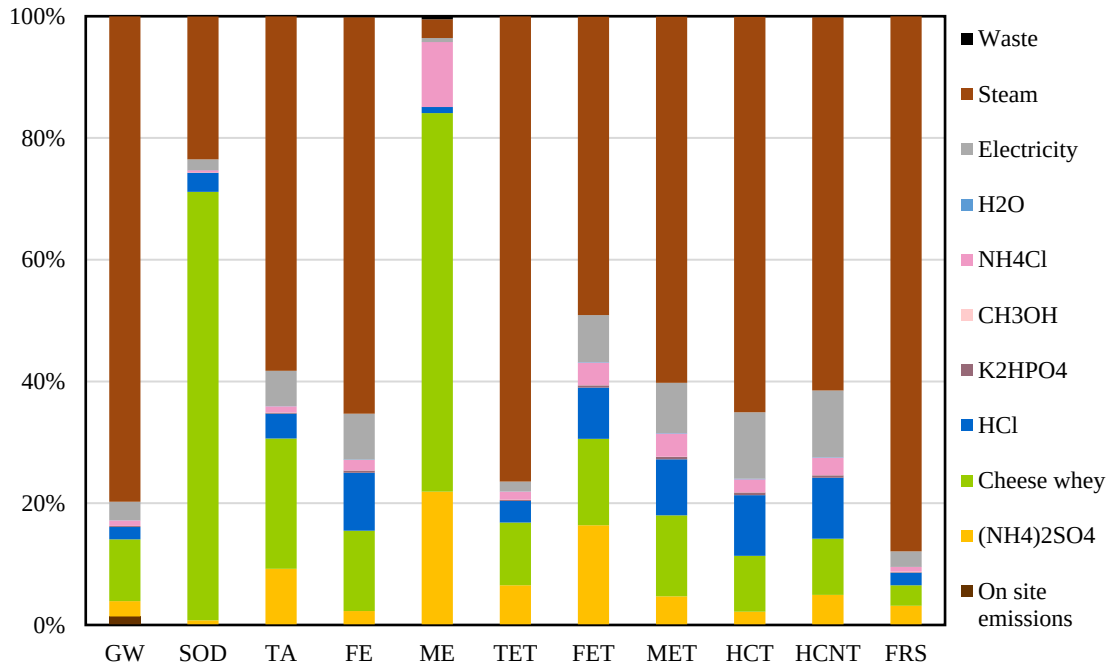

Figure 2. Environmental profile of nisin and lactic acid co-production using CW as substrate.

In order to provide an improved scenario, a sensitivity analysis is developed, based on the previously identified hot spots. In the case of cheese whey, it could be thought that, with the improvement and optimization of the process, less quantity of raw material is needed for the production of nisin, thus allowing to reduce the environmental burdens associated. To this end, a 5%-10% reduction in the amount of cheese whey required is analyzed, seeking to identify the potential of this process optimization alternative.

On the other hand, in the same line of improving the efficiency and productivity of the biotechnological process, a reduction of the ammonium sulfate requirements could also be achieved. The reduction in the dosage of this compound is barely equal to that considered for cheese whey, in the range of 5%-10%.

Lastly, in the case of steam, two main approaches could be considered aiming to provide an improved environmental profile: (1) reduction on the amount of steam required by 10%-20%, this could be achieved by developing a Pinch analysis for the different streams of the process, and (2) promoting the use of steam from renewable resources.

Bearing the alternative scenarios mentioned above, a series of actions are proposed to improve the environmental profile (**Figure 3**). In the case (1) a reduction in the cheese whey dosage is evaluated, for alternative (2) a minimization in the use of ammonium sulfate is analyzed, in case (3) the two options for steam are evaluated and finally, case (4) introduces the optimized scenario considering the three alternatives.

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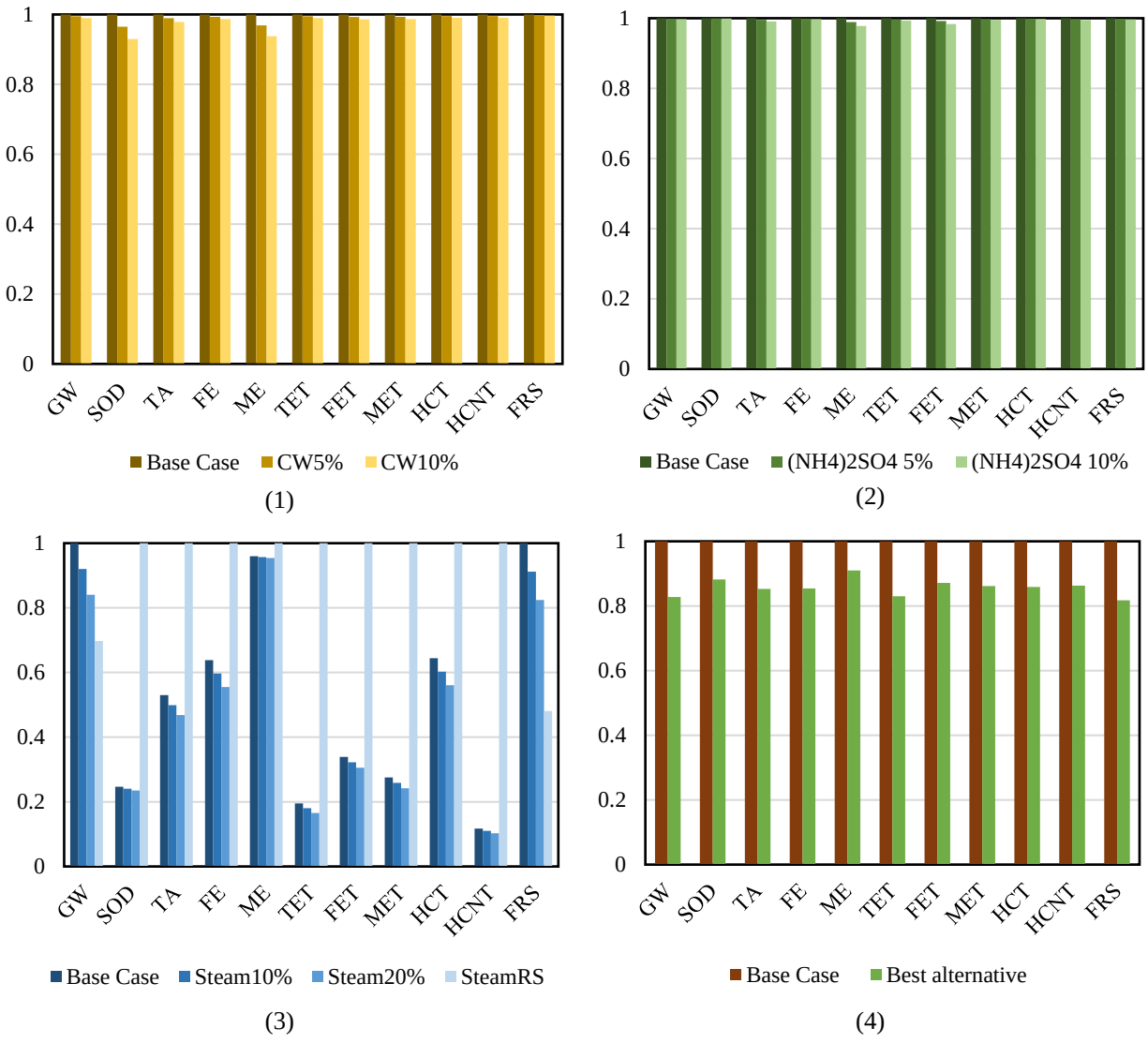

Figure 3. Sensitivity assessment of the environmental profile of cheese whey valorisation

As can be seen, the optimization of steam requirements is the one that promotes a better environmental profile, achieving a reduction of the impacts that amounts to 50% in the case of the FRS category, when an alternative renewable source is used as steam feedstock, and 31% for the GW impact category. However, it should be noted that, although in both impact categories the loads are significantly reduced, the same is not true for the others, as an increase is observed when wood residues are used for steam production. In this sense, it could be concluded that the optimization of steam requirements throughout the process is the preferred scenario, since reduced environmental loads, in the order of 10-18%, are obtained. For cases (1) and (2) the reduction on the environmental loads is not so noticeable, for (1) only in the impact categories of SOD and ME an impact reduction of around 10% is achieved, while for (2) the most reduced load is observable for the ME category, amounting to 3%.

On the other hand, as it is expected that the alternative improvement scenarios based on the hotspots identified for the base case could be integrated in order to provide the "best alternative" possible, case (4) has also been analyzed. For this scenario, the best scores obtained

for the three previous scenarios were considered, considering that in the case of steam, a 20% reduction is the best option. Accordingly, the range of environmental load reduction is between 10%-18%.

8.5.2 **Scenario II. Sugar beet pulp valorization.**

Table 4 includes the summary of the data used for the modeling of Scenario II of sugar beet pulp valorization according to the mass and energy balances.

Table 4. Main inventory data for the biotechnological valorization of SBP residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	615.43	kg	Nisin	3.94	g
Ammonium Sulfate	0.41	kg	Lactic acid	96.06	g
Enzymes	40.49	g	*Total*	*1.00*	*kg*
HCl	0.46	kg			
K_2HPO_4	1.58	kg	*Emissions to air*		
Magnesium Sulfate	31.61	g	Carbon dioxide	1.68	kg
Methanol	31.97	g	Water, vapour	11.68	kg
SBP	11.49	kg			
NH_4OH	0.32	kg			
Sulfuric Acid	0.23	kg			
Water	2.07	kg			
Electricity/heat			*Waste to treatment*		
Cooling water	0.78	m^3	Slurry	1.83	kg
Steam	158.24	kg	Final waste	1.32	kg
Energy	5.98	kWh			

Figure 4 includes the environmental profile of the manufacturing process using SBP as a carbon source. The profile shows that energy needs make the greatest contribution, representing more than 50% of the impact value in almost all the categories studied. However, three exceptions could be identified, namely in the ME and SOD categories, where it is sugar beet pulp that accounts for the largest environmental burden.

The relevance of background activities associated with SBP on impact categories SOD and ME show that agricultural activities are the main contributors in the environmental profile, which is attributed to field emissions resulting from the application of fertilizers and agrochemicals. On the other hand, the use of fuel and electricity required for crop processing also has some contribution within the TA category, due to the release of acidifying substances.

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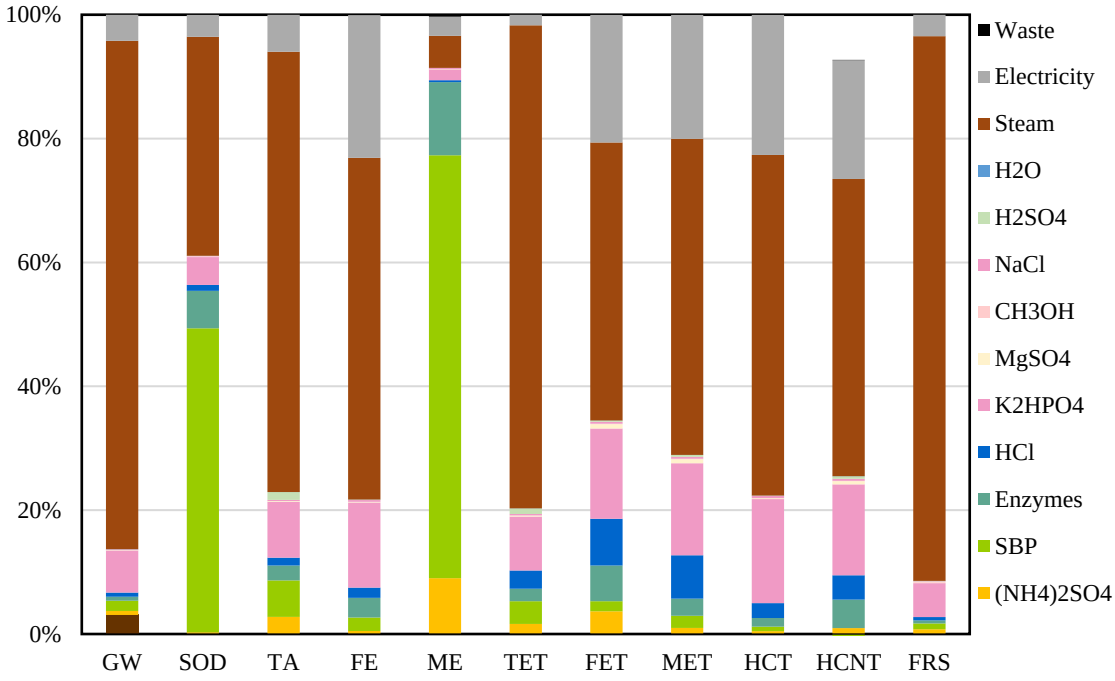

Figure 4. Environmental profile of nisin and lactic acid co-production using SBP as substrate.

In order to provide an improved scenario, a sensitivity analysis is developed, based on the hotspots previously identified. In the case of SBP, it could be thought that, with the improvement and optimization of the process, less quantity of raw material is needed for the production of nisin, thus allowing to reduce the environmental loads associated with its use. To this end, a 5%-10% reduction in the amount of SBP required is analyzed, seeking to identify the potential of this process optimization alternative. For electricity 10%-20% of diminishment in the amount of utility required has been assessed, with the alternative of using renewable electrical energy. In this case, the idea is to provide a "new electricity mix", considering only the use of renewable resources, mainly from hydropower, wind and solar panels. Same approaches has been considered for steam.

Bearing the alternative scenarios aforementioned, the following environmental profile improvement is obtained (**Figure 5**). In the case (1) a reduction on the dose of sugar beet pulp is evaluated, for alternative (2) a minimization on the use of electricity is analyzed, in the case (3) the two options for steam are evaluated and finally, case (4) introduces the optimized scenario considering the three alternatives.

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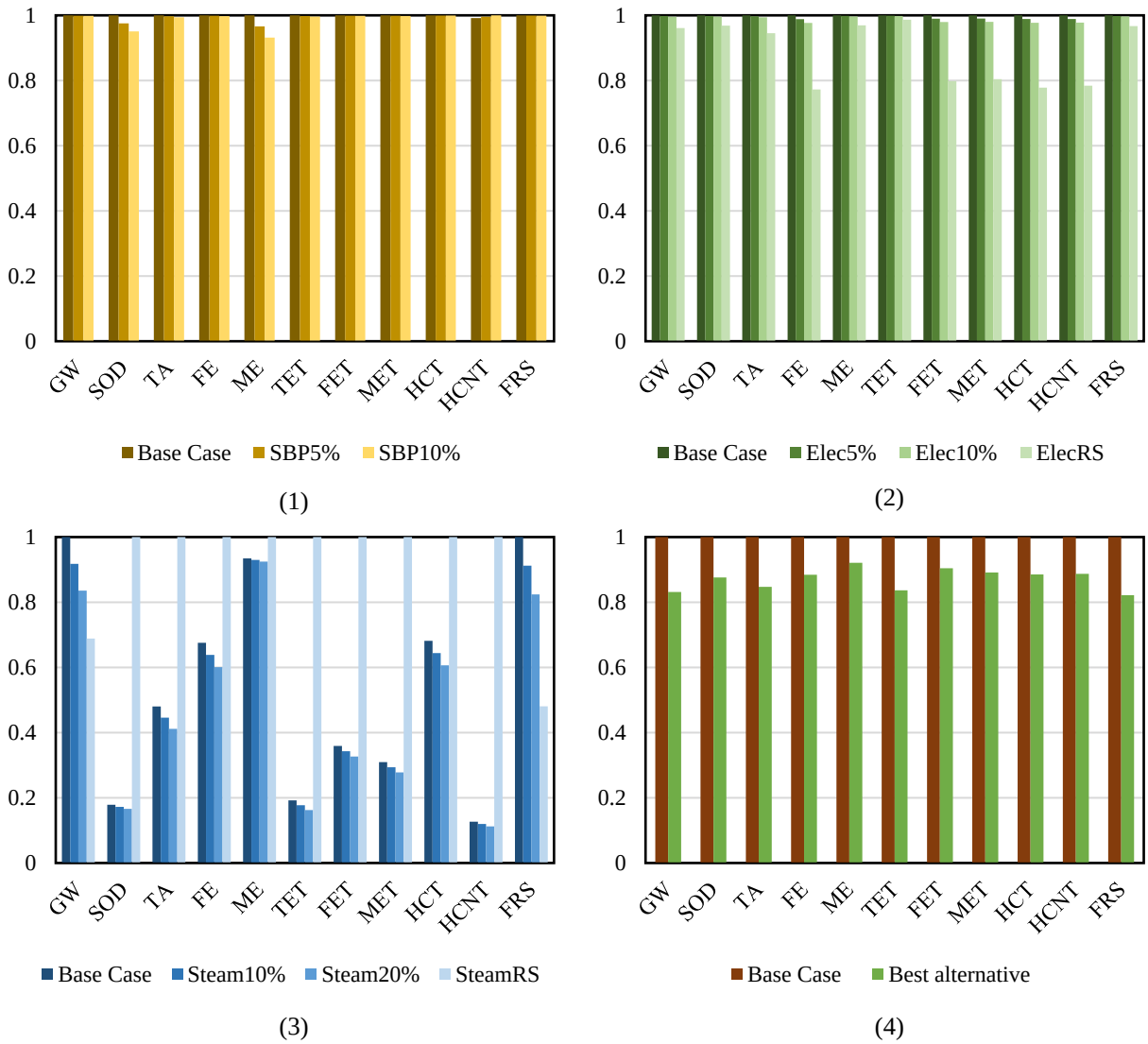

Figure 5. Sensitivity assessment of the environmental profile of SBP valorisation

As can be seen, the optimization of steam requirements is the one that promotes a better environmental profile, achieving impact loads with a reduction range that amounts to 52% in the case of the FRS category and 32% for the GW impact category. However, although the loads of these two impact categories are significantly reduced, the same is not true for the others, as an increase is observed when wood residues are used for steam production. In this sense, it can be concluded that, for this alternative scenario, in general, the optimization of the steam requirements throughout the process is the preferred scenario, since reduced environmental loads are obtained, in the range of 9-18%.

For case (1) the reduction in environmental burdens is not so evident, since only in the SOD and ME impact categories is an impact reduction of around 6% achieved. But for case (2) the impact reduction capacity is significantly high. The alternative scenario that provides the best results is the one derived from the use of renewable resources for electricity production. The reduction of the impact on the environment could amount to 20%-23%, for the case of all

impact categories related to toxicity, with the exception of TET, and also for FE. On the other hand, the reduction of electricity requirements as a result of process optimization could lead to a reduction of the environmental burden in the order of 4% for the toxicity-related impact categories and less than 3% for the rest.

Considering the scores obtained, there is a need of process optimization based on the reduction of the electricity needs, given its huge contribution over the environmental profile, or, as alternative, promote the use of renewable resources for its production.

On the other hand, as it is expected that alternative improvement scenarios based on the conflict points identified for the base case can be integrated to provide the "best alternative" possible, case (4) has also been analyzed. For this scenario, the best scores obtained for the three previous scenarios have been taken into account, considering that for electricity the use of renewable resources is encouraged and, for steam, a 20% reduction over its requirements is the best option. Accordingly, the range of reduction of environmental loads is between 5%-18%, which is considered an acceptable scale of improvement.

8.5.3 **Scenario III. Corn stover valorization.**

The summary of the data used for the modelling of Scenario III on the valorization of corn stover is included in **Table 5**, including all the inputs and outputs related with the process of corn stover valorization.

Table 5. Main inventory data for the biotechnological valorization of CS residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	756.31	kg	Nisin	4.28	g
Ammonium Sulfate	0.45	kg	Lactic acid	95.72	g
Enzymes	9.53	kg	*Total*	*1.00*	*kg*
HCl	3.73	kg			
K_2HPO_4	1.15	kg	*Emissions to air*		
Magnesium Sulfate	34.64	g	Carbon dioxide	1.81	kg
Methanol	51.04	g	Water, vapour	97.27	kg
CS	10.40	kg			
NH_4OH	0.35	kg			
Sulfuric Acid	0.21	kg			
Water	95.03	kg			
Electricity/heat			*Waste to treatment*		
Cooling water	22.95	m^3	Slurry	17.65	kg
Steam	123.52	kg	Final waste	4.73	kg
Energy	21.36	kWh			

Figure 6 includes the environmental profile of the manufacturing process using CS as a carbon source. The profile reflects that the use of enzymes for saccharification of corn stover has the highest contribution, representing more than 60% of the impact value in almost all the categories studied. This intense impact on the profile makes it necessary to carry out an analytical study to identify the rationale behind it. For this purpose, the background of the activities associated with enzyme production has been analyzed, in which it has been identified that energy requirements and the production of fermentable sugars for enzyme production, are the main hot spots.

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In addition, it is worth mentioning that the energy requirements of the process, electricity and steam, also have some impact on the environmental profile, highlighting the FRS categories, given the consumption of non-renewable fossil resources for energy production, and GWP, contribution resulting from the emissions derived from their production processes.

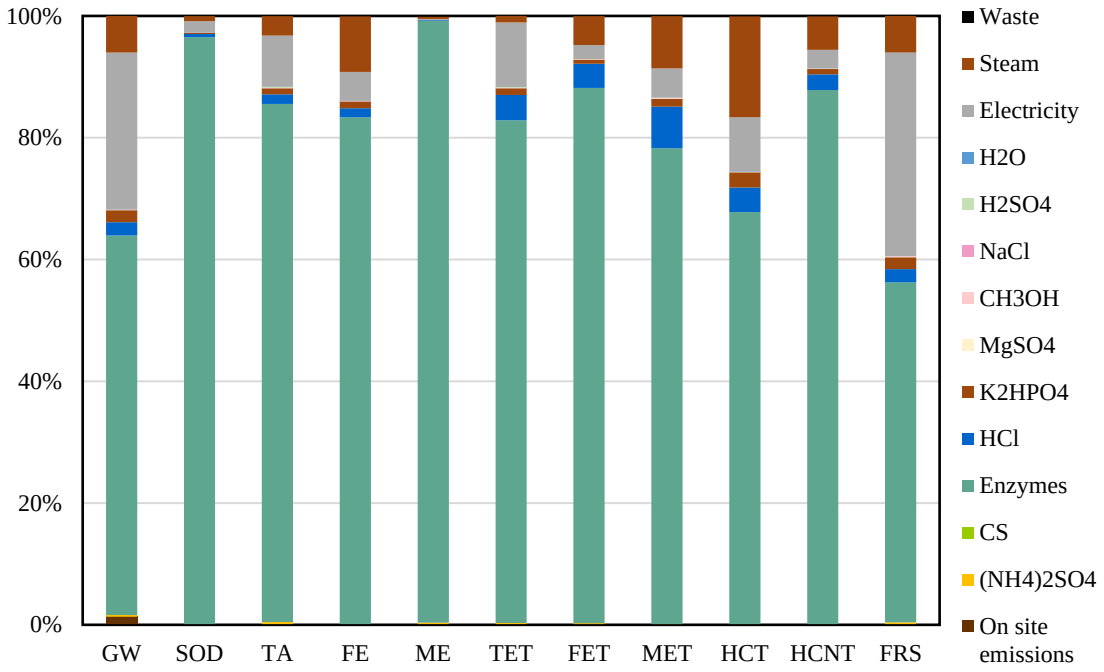

Figure 6. Environmental profile of nisin and lactic acid co-production using CS as substrate.

As made for the previous scenarios, in order to provide an improved alternative, a sensitivity analysis has been developed, based on the main hotspot previously identified. To this end, a reduction of 5%-10% in the amount of enzyme dose required is analyzed, seeking to identify the potential of this process optimization alternative. This reduction is expected to be achieved by increasing the productivity of the process: if the process is more optimized, it is expected to obtain a higher amount of nisin using the same amount of feedstock (corn stover), which implies a lower involvement of the pretreatment section, where the enzymes are used, especially the environmental profile. In this regard, only one alternative is provided within the sensitivity analysis, depicted in **Figure 7**.

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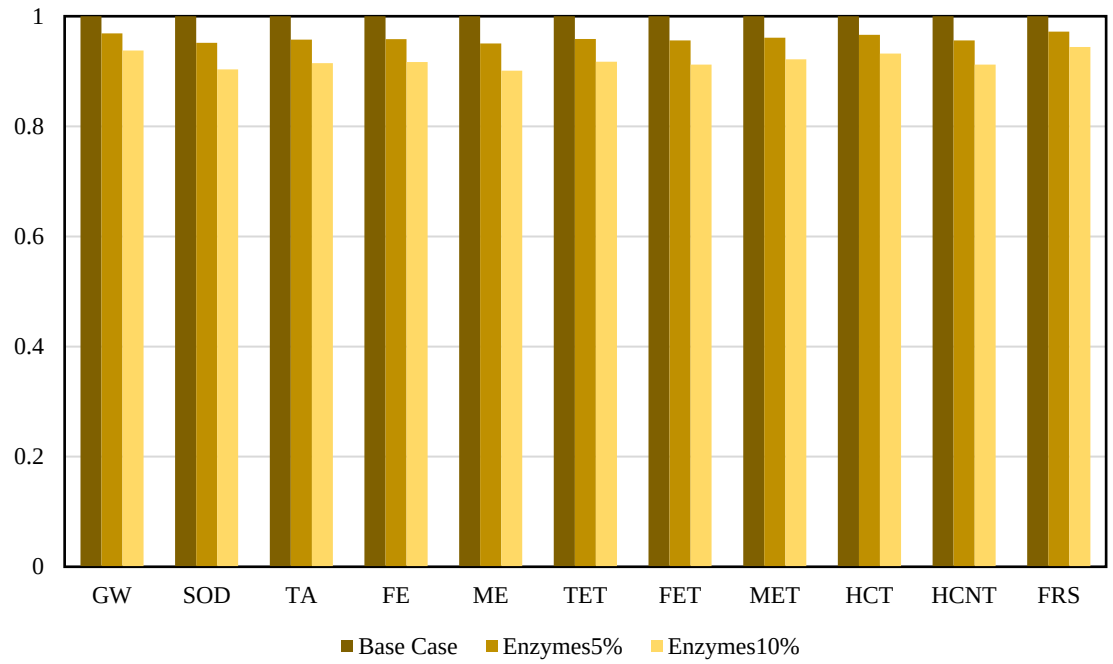

Figure 7. Sensitivity assessment of the environmental profile of SBP valorization

Considering this improved alternative scenario, the reduction on the environmental burden could reach 10% for the SOD and ME impact categories, followed by 8%-9% with the categories related to toxicity and fossil resource, while for the rest, less than 7% profile improvement is obtained. Although the results are not as significant as in the previous scenarios, it is shown that by optimizing the process in the use of enzymes, environmental impacts could be reduced and thus provide a more sustainable nisin production scenario.

8.6 Comparison of the damage potential of each alternative

Evaluating the values obtained through the Recipe Endpoint methodology (**Figure 8**), it is concluded that the co-production of nisin and lactic acid that results in the least damage potential is the one that uses SBP as a substrate. Another significant aspect of the results obtained is that, according to this methodology, the Human Health damage category is the most affected, since its value is almost three times higher than that obtained for the Ecosystem Quality and Resource Scarcity damage categories. The use of fewer chemicals, the efficient use of energy and the use of renewable energy resources would reduce the damage value obtained for this impact category, in turn reducing the overall damage value associated with the processes. Therefore, the optimization of the production process would be necessary in order to improve the overall environmental quality of the processes.

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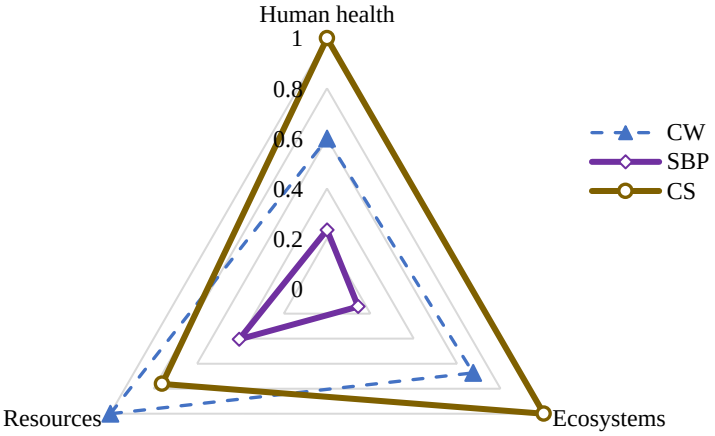

Figure 8. Damage potential values obtained by applying Recipe EndPoint methodology to the proposed alternatives.

8.7 Mass & Economic allocation

The values considered to perform the mass and economic allocation are those included in **Table 6**. As it has been included in the table referring to the production capacities of the processes (**Table 1**), the amount of lactic acid produced annually is significantly higher than the amount of nisin generated, which will mean that when making the allocation of mass and evaluate the environmental impacts associated with nisin, these will be much lower than those corresponding to the production of lactic acid. On the other hand, the market value of nisin, given its wide potential for use in the sector of food and pharmaceuticals, is much higher compared to that of lactic acid. This fact will lead to the fact that, when conducting an environmental analysis taking into account an economic allocation, the contribution of nisin to the environmental impacts derived from the production process will be greater to the consideration of a mass-based allocation.

But even so, an allocation percentage of more than 41.19% will not be achieved for nisin, even considering its monetary market value, since the production capacity of nisin is much lower than that of lactic acid (**Table 1**). Given the greater accessibility of nisin production from cheese whey thanks to the fact that this substrate can be used directly in fermentation without the need for pretreatment for the release of fermentable sugars (since lactose is already freely present in its composition), the value of the percentage contribution of nisin, considering both the mass and economic allocations, is the highest of the three alternatives considered. This is favorable in productive and economic terms, since there is a higher production capacity of the coproduct with higher potential and higher market value, but it is unfavorable in terms of the environmental impacts generated, since the nisin produced from CW will have a higher contribution compared to the use of SBP or CS as substrates.

Thus, globally it could be considered that the contribution of lactic acid production to the environmental impacts generated by all the productive processes studied is greater in comparison with that of nisin. This statement could be verified with the values reported in **Table 6**, which refer to the contribution of nisin on the environmental results for the three process alternatives for each of the impact categories of the ReCiPe MidPoint methodology.

Table 6. Mass and economic allocation considering the three types of feedstocks.

Cheese whey		MA		EA	
		Nisin	**LA**	**Nisin**	**LA**
GW	kg CO_2 eq	$1.14 \cdot 10^{1}$	$1.25 \cdot 10^{2}$	$5.63 \cdot 10^{1}$	$8.03 \cdot 10^{1}$
SOD	kg CFC_{11} eq	$9.40 \cdot 10^{-6}$	$1.04 \cdot 10^{-4}$	4.66E-05	6.65E-05
TA	kg SO_2 eq	$3.46 \cdot 10^{-2}$	$3.81 \cdot 10^{-1}$	$1.71 \cdot 10^{-1}$	$2.45 \cdot 10^{-1}$
FE	kg P eq	$1.73 \cdot 10^{-3}$	$1.91 \cdot 10^{-2}$	$8.58 \cdot 10^{-3}$	$1.23 \cdot 10^{-2}$
ME	kg N eq	$1.79 \cdot 10^{-3}$	$1.98 \cdot 10^{-2}$	$8.89 \cdot 10^{-3}$	$1.27 \cdot 10^{-2}$
TET	kg 1.4-DCB	$1.65 \cdot 10^{1}$	$1.82 \cdot 10^{2}$	$8.20 \cdot 10^{1}$	$1.17 \cdot 10^{2}$
FET	kg 1.4-DCB	$5.38 \cdot 10^{-2}$	$5.94 \cdot 10^{-1}$	$2.67 \cdot 10^{-1}$	$3.81 \cdot 10^{-1}$
MET	kg 1.4-DCB	$7.13 \cdot 10^{-2}$	$7.87 \cdot 10^{-1}$	$3.53 \cdot 10^{-1}$	$5.05 \cdot 10^{-1}$
HCT	kg 1.4-DCB	$9.26 \cdot 10^{-2}$	1.02	$4.59 \cdot 10^{-1}$	$6.55 \cdot 10^{-1}$
HCNT	kg 1.4-DCB	2.27	$2.51 \cdot 10^{1}$	$1.13 \cdot 10^{1}$	$1.61 \cdot 10^{1}$
FRS	kg oil eq	3.59	$3.96 \cdot 10^{1}$	$1.78 \cdot 10^{1}$	$2.54 \cdot 10^{1}$
Sugar beet pulp		MA		EA	
		Nisin	**LA**	**Nisin**	**LA**
GW	kg CO_2 eq	2.16	$5.02 \cdot 10^{1}$	$1.32 \cdot 10^{1}$	$4.16 \cdot 10^{1}$
SOD	kg CFC_{11} eq	$1.22 \cdot 10^{-6}$	$2.84 \cdot 10^{-5}$	$7.46 \cdot 10^{-6}$	$2.36 \cdot 10^{-5}$
TA	kg SO_2 eq	$5.54 \cdot 10^{-3}$	$1.29 \cdot 10^{-1}$	$3.38 \cdot 10^{-2}$	$1.07 \cdot 10^{-1}$
FE	kg P eq	$4.00 \cdot 10^{-4}$	$9.30 \cdot 10^{-3}$	$2.44 \cdot 10^{-3}$	$7.71 \cdot 10^{-3}$
ME	kg N eq	$2.09 \cdot 10^{-4}$	$4.87 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$4.03 \cdot 10^{-3}$
TET	kg 1.4-DCB	3.17	$7.38 \cdot 10^{1}$	$1.94 \cdot 10^{1}$	$6.11 \cdot 10^{1}$
FET	kg 1.4-DCB	$1.15 \cdot 10^{-2}$	$2.68 \cdot 10^{-1}$	$7.03 \cdot 10^{-2}$	$2.22 \cdot 10^{-1}$
MET	kg 1.4-DCB	$1.65 \cdot 10^{-2}$	$3.83 \cdot 10^{-1}$	$1.00 \cdot 10^{-1}$	$3.17 \cdot 10^{-1}$
HCT	kg 1.4-DCB	$2.14 \cdot 10^{-2}$	$4.98 \cdot 10^{-1}$	$1.31 \cdot 10^{-1}$	$4.12 \cdot 10^{-1}$
HCNT	kg 1.4-DCB	$4.86 \cdot 10^{-1}$	$1.13 \cdot 10^{1}$	2.97	9.36
FRS	kg oil eq	$7.03 \cdot 10^{-1}$	$1.64 \cdot 10^{1}$	4.29	$1.35 \cdot 10^{1}$
Corn stover		MA		EA	
		Nisin	**LA**	**Nisin**	**LA**
GW	kg CO_2 eq	5.84	$1.31 \cdot 10^{2}$	$3.51 \cdot 10^{1}$	$1.01 \cdot 10^{2}$
SOD	kg CFC_{11} eq	$1.96 \cdot 10^{-5}$	$4.39 \cdot 10^{-4}$	$1.18 \cdot 10^{-4}$	$3.41 \cdot 10^{-4}$
TA	kg SO_2 eq	$3.97 \cdot 10^{-2}$	$8.88 \cdot 10^{-1}$	$2.38 \cdot 10^{-1}$	$6.89 \cdot 10^{-1}$
FE	kg P eq	$3.91 \cdot 10^{-3}$	$8.75 \cdot 10^{-2}$	$2.35 \cdot 10^{-2}$	$6.79 \cdot 10^{-2}$
ME	kg N eq	$6.40 \cdot 10^{-3}$	$1.43 \cdot 10^{-1}$	$3.84 \cdot 10^{-2}$	$1.11 \cdot 10^{-1}$
TET	kg 1.4-DCB	$1.98 \cdot 10^{1}$	$4.43 \cdot 10^{2}$	$1.19 \cdot 10^{2}$	$3.44 \cdot 10^{2}$
FET	kg 1.4-DCB	$1.93 \cdot 10^{-1}$	4.31	1.16	3.35
MET	kg 1.4-DCB	$1.49 \cdot 10^{-1}$	3.32	$8.93 \cdot 10^{-1}$	2.58
HCT	kg 1.4-DCB	$1.13 \cdot 10^{-1}$	2.53	$6.79 \cdot 10^{-1}$	1.96
HCNT	kg 1.4-DCB	7.64	$1.71 \cdot 10^{2}$	$4.59 \cdot 10^{1}$	$1.33 \cdot 10^{2}$
FRS	kg oil eq	1.57	$3.51 \cdot 10^{1}$	9.42	$2.72 \cdot 10^{1}$

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8.8 Outcomes of the economic assessments

The economic assessment has been applied to the scenarios of CW, SBP and CS. Taking into account all the considerations described for the performance of the economic analysis, the values obtained are shown in **Table 7**.

Table 7. Economic parameters obtained by performing the economic evaluation of the biotechnological production process of nisin and lactic acid using CW, SBP and CS as substrates.

Economic Parameters	CW	SBP	CS
Total Investment [€]	33 715 000	52 222 000	27 080 000
Fixed Capital [€]	32 029 000	49 629 000	25 164 000
1. Total Plant Direct Cost [€]	27 611 000	42 784 000	21 693 000
2. Total Plant Indirect Cost [€]	4 418 000	6 845 000	3 471 000
Labor Cost [€/year]	253 808	870 286	585 914
Material Cost [€/year]	81 280	129 311	6 008 225
Utilities Cost [€/year]	592 640	338 692	640 902
Annual Operation Cost [€/year]	2 222 000	3 367 000	8 271 000
Revenues [€/year]	5 259 823	11 105 971	3 577 306
1. Nisin [€/year]	2 166 441	2 689 412	926 619
2. Lactic Acid [€/year]	3 093 382	8 416 559	2 650 687
Gross Profit [€/year]	3 038 000	7 739 000	-4 694 000
Net Profit [€/year]	2 279 000	5 804 000	-4 694 000
Gross Margin [%]	57.76	69.68	-131.20
Return on Investment [%]	6.76	11.11	-17.33
Payback Time [years]	14.80	9.00	N/A
Net Present Value [€]	14 386 000	68 556 000	-116 455 000

The economic indicators showed that the proposed manufacturing processes are economically viable in the case of CW and SBP substrates, since the Net Present Values (NPV) are positive. On the contrary, in the case of the CS substrate, the negative NPV value reflects that the total revenues obtained during the life of the project considered (30 years) is not sufficient to take over all the manufacturing and investments cost associated with the process. In more detail, the item of material costs presents very different values, compared to the CW and SBP process. A percentage of 99% of the material cost of the CS process is related to the amount of enzymes needed for the saccharification stage, as can be seen in Table 4 (9.53 kg of enzymes/kg of products obtained). As the prices of the enzymes are high (around 2.47 €/kg), their contribution to the economic performance will also be significant. Thus, the economic viability of the CS process could be achieved if the amount of enzymatic materials needed for saccharification is optimized (and reduced).

On the other hand, regarding CW and SBP processes, the economic parameters of Return on Investment (6.67 and 11.11 respectively) and Payback time (14.80 and 9.00 respectively), reflect that the necessary investment for the development of the manufacturing processes is reasonable, leading to good alternatives for the co-production of nisin and lactic acid from waste streams, promoting in this way the circular economy concept.

8.9 Eco-efficiency analysis of the alternatives

Looking to provide an additional analysis method for the comparison of scenarios, the eco-efficiency analysis (EEA) methodology has been used. According to the ISO 14046 guidelines, the indexes considered for assessment are related with the economic and environmental pillars, being the costs, profits and production capacity, the ones embedded on the economic aspect, and the impact loads obtained by the LCA methodology the ones used for the environmental approach. The EEA index values obtained are shown in **Table 8**, the CS scenario has not been taken into account in this evaluation since it is not economically feasible.

Table 8. EEA indexes obtained for CW and SBP scenarios. Acronym EI refers to Environmental Impact.

Index	**€/impact**		**€/ impact**		**kg products / impact**	
Variables	Net profit/EI		Production costs/EI		Production capacity/EI	
	CW	SBP	CW	SBP	CW	SBP
GW	0.05	0.13	0.76	1.14	0.01	0.02
SOD	$6.57 \cdot 10^4$	$2.35 \cdot 10^5$	$9.24 \cdot 10^5$	$2.01 \cdot 10^6$	$8.84 \cdot 10^3$	$3.22 \cdot 10^4$
TA	17.86	51.80	251	442	2.40	7.11
FE	357	718	$5.01 \cdot 10^3$	$6.14 \cdot 10^3$	48.0	98.5
ME	344	$1.37 \cdot 10^3$	$4.84 \cdot 10^3$	$1.17 \cdot 10^4$	46.4	188
TET	0.04	0.09	0.52	0.77	0.01	0.01
FET	11.47	24.92	161	213.08	1.54	3.42
MET	8.66	17.44	122	149	1.17	2.39
HCT	6.67	13.41	93.74	115	0.90	1.84
HCNT	0.27	0.59	3.81	5.05	0.04	0.08
FRS	0.17	0.41	2.42	3.49	0.02	0.06

In the same context, **Figure 9**, **Figure 10** and **Figure 11** include the eco-efficiency graphs on the most representative impact categories, considering first the net profit versus environmental load, followed by the indexes obtained by evaluating production costs and production capacity in relation to environmental impacts. The graphs are divided into four main quadrants, which are constructed from the mean values of each variable included in the graph. The eco-efficient region is represented by green, while the non-eco-efficient with red, being the yellow region the one representative of an intermediate position.

Bearing in mind that "as much net profit and reduced environmental load, more eco-efficient alternative scenario, and viceversa", it could be seen that, considering the GWP impact category, the use of SBP as feedstock is more eco-efficient, as higher profit and lower carbon footprint is obtained (**Figure 9**). The same tendency is observed for the FE impact category, which is in line with the results obtained following the LCA methodology. On the other hand, it should be taken into account that in the case of FE, in the CW alternative the "distance" with the intermediate position (yellow backgrounds) is lower to that of the GW impact category, thus implying that the need of improvement of the scenario is not as intense in comparison.

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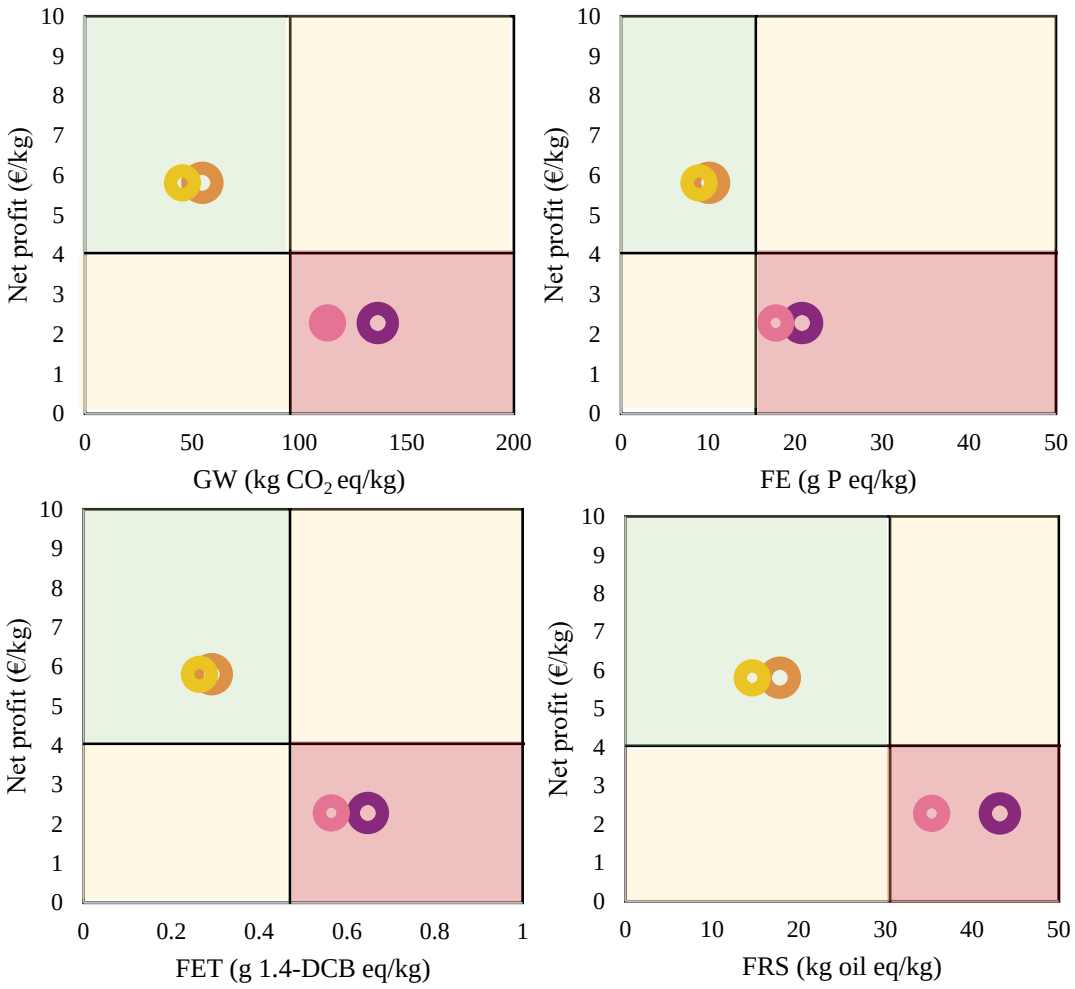

Figure 9. Eco-efficiency analysis considering the index between the net profits of the biotechnological production scheme and the environmental loads. Color code: ● CW base scenario, ● CW optimized scenario, ● SBP base scenario, ● SBP optimized scenario.

In the case of the index relating production costs to environmental impacts, the reasoning shifts to "as lower production costs and reduced environmental loads, more eco-efficiency achieved, and viceversa". As shown on **Figure 10** none of the scenarios are in the eco-efficient quadrant (green), but neither are they in the non-eco-efficient quadrant (red), which can be considered as a high potential for the scenarios to improve their processes in the search for eco-efficiency in the production chain. However, it is important to mention that the fact of developing an emerging production scheme, using biological and residual raw materials, implies that its degree of optimization is at very low values, which has a high impact on the total costs of the process, higher compared to other more traditional processes. For this reason, it is expected to obtain these indexes.

Furthermore, it is observed that the sensitivity scenarios, where the aim is to reduce the impact of those variables with a greater environmental contribution on the process profile, present a result that is closer to an "eco-efficient" production model. This fact is observed

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especially in the TET and FRS categories of the CW process, where the greatest difference between the base scenario and the optimized scenario is observed.

On the other hand, in order to improve the results obtained, for the SBP scenario, a reduction in production costs would imply a closer approach to an eco-efficient system, while for the CW scenario, the focus should be on reducing the associated environmental impacts.

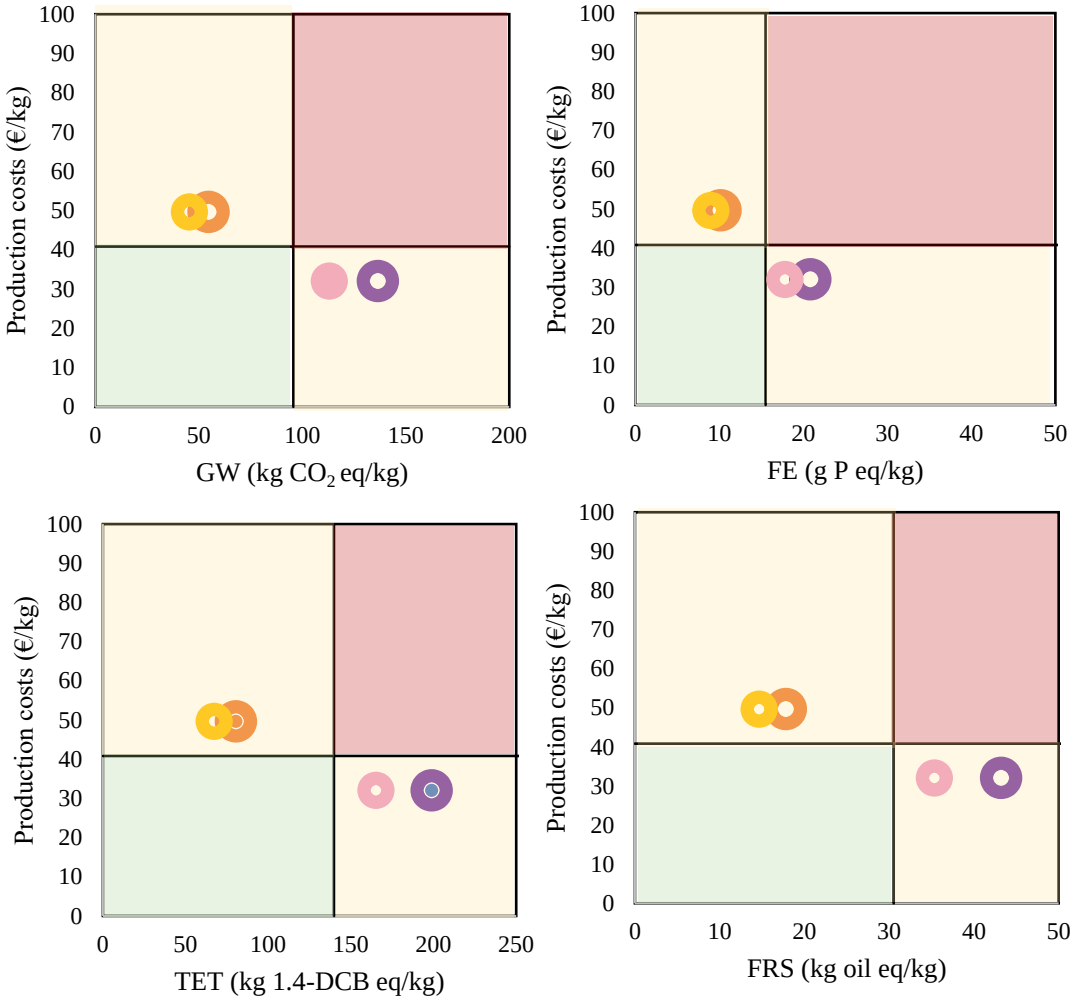

Figure 10. Eco-efficiency analysis considering the index between the production costs of the biotechnological production scheme and the environmental loads. Color code: ● CW base scenario, ● CW optimized scenario, ● SBP base scenario, ● SBP optimized scenario.

The last index analyzed is the one that considers the production capacity of the installation and the environmental loads associated, to this end, in this case "as higher production capacity and lower environmental loads, more eco-efficient scenario, and viceversa". As depicted in **Figure 11** the results obtained are analogous to that of **Figure 10**, being the SBP scenario the one that is considered eco-efficient, given its high productivity of the process, leading to a higher production capacity, and its lower environmental loads, in comparison to that of CW.

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On the other hand, as in the previous case, the degree of improvement by considered an optimization on the variables that contributes the most over the environmental profile is significantly observable for the CW scenario on the GW and FRS impact categories, which is indicative of the CW scenario's ability to evolve towards a more eco-efficient production model.

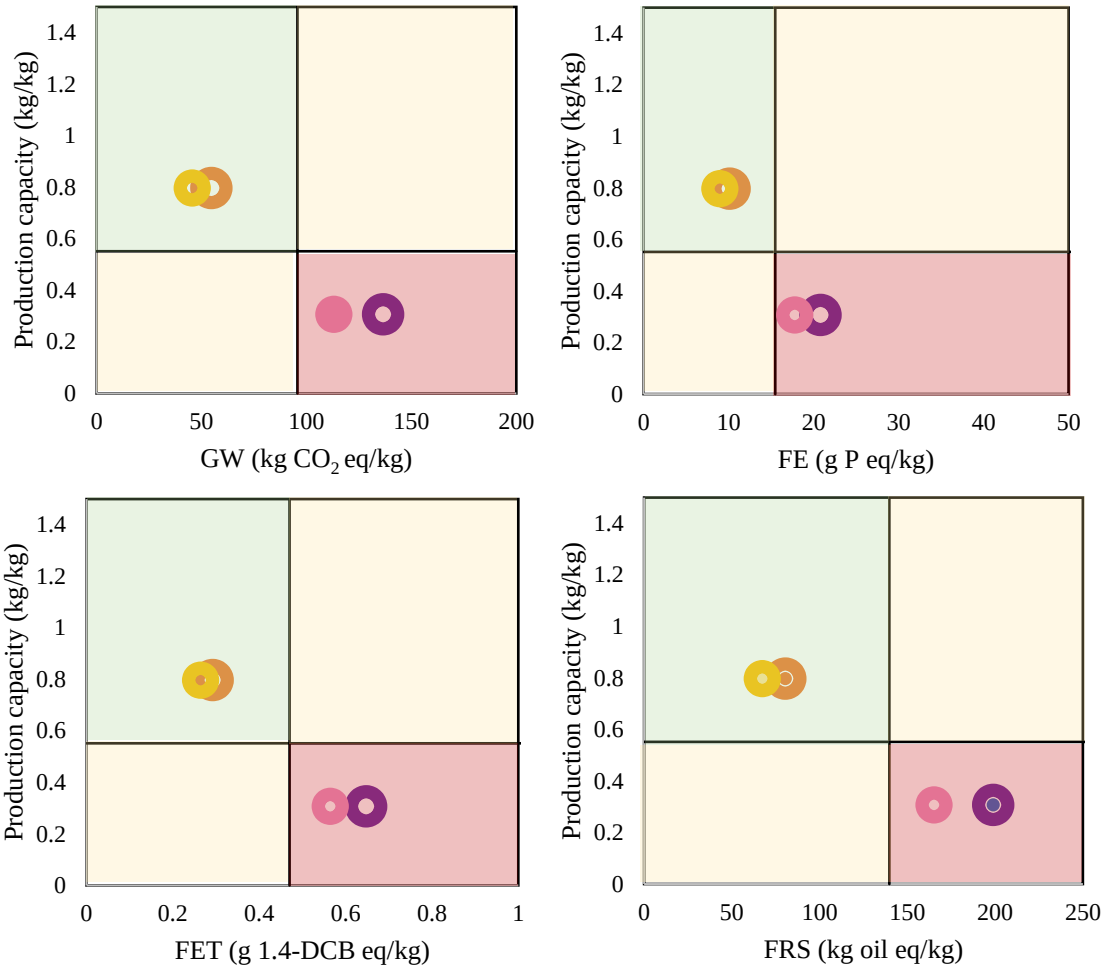

Figure 11. Eco-efficiency analysis considering the index between the production capacity of and the environmental loads. Color code: ● CW base scenario, ● CW optimized scenario, ● SBP base scenario, ● SBP optimized scenario.

8.10 Greenness Grid methodology

To obtain the score of the Green Index, aiming to evaluate the degree of "green process" and its actual potentiality, the development of a series of stets is required, based on the principles of Green Chemistry. **Table 9** includes the main results obtained for the scenarios evaluated, in which the value of 0 represent the worst sustainable score, while the value of 1 the highest possible.

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Table 9. Metric scores values and global Green Index obtained for CW, SBP and CS scenarios**.**

	Metric	CW	SBP	CS		Metric	CW	SBP	CS
1	E factor	0.64	0.93	0.62	**9**	Catalyst	0.00	0.00	0.00
2	Atom Economy	1.00	1.00	1.00	**10**	Degradability	1.00	1.00	1.00
3	Process Safety	0.50	0.50	0.50	**11**	Safety	0.98	0.98	0.98
4	Reduced Toxicity	1.00	1.00	1.00	**12**	Accident Prevention	0.75	0.75	0.75
5	Safe Solvents	0.98	0.98	0.98	**13**	Carbon Efficiency	1.00	1.00	1.00
6	Energy Efficiency	0.11	0.38	0.03	**14**	Reaction Efficiency	0.00	0.00	0.00
7	Renewable Resources	0.99	0.98	1.00	**15**	Mass Productivity	1.00	0.95	0.80
8	Avoided Derivatives	0.50	0.50	0.50	**GREEN INDEX**		**10.45**	**10.95**	**10.16**

According to this methodology, the differences between the scenarios are not so significant, with the SBP process scheme being the one that achieves a higher green index value, thus being considered as the "best" alternative scenario. Since the equipment and process steps are similar among them, no major differences are detected in the metrics evaluated, with the exception of metric 6 "Energy Efficiency", which represents the energy requirements and associated environmental costs (considering global warming potential as the main impact category), for which the CS scenario is significantly inefficient, while the SBP is 10 times more efficient, but still insufficient, and metric 1 "E-Factor", which is calculated as the mass of waste produced per kg of product obtained, the higher the ratio, the lower the value of the score. Again, the SBP production scheme is more adequate in terms of resource recovery and waste production reduction, while the CW and CS scenarios are in line with each other.

On the other hand, in order to identified which is the degree of improvement needed for each scenario, the **Figure 12** is depicted. Considering that 15 is the maximum score (represented by the green line) to be obtained, the SBP scenarios need to improve by 27.1%, while the CS and CW process schemes need to increase their efficiency by 32.3% and 30.3%, respectively.

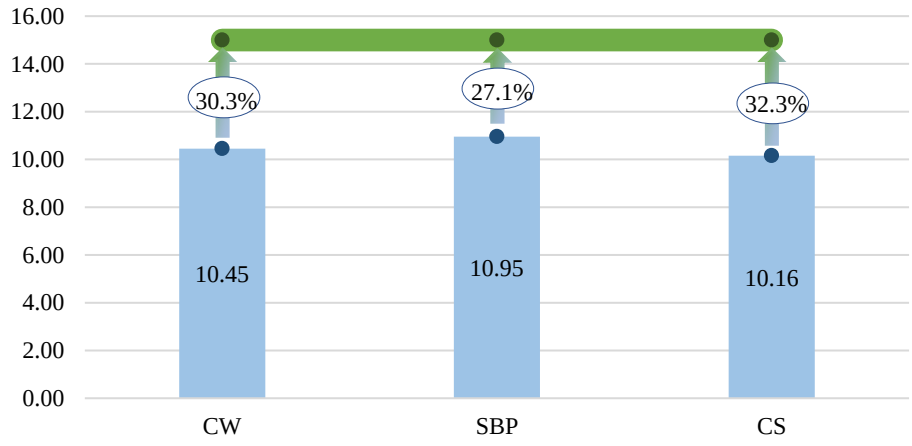

Figure 12. Green Index score and degree of improvement needed to achieve the highest Green Index value.

8.11 Conclusions

The scores obtained suggest that the valorization of cheese whey is the one that leads to the higher nisin production per batch process, although, on the other hand, when assessing the economic feasibility of this alternative and the potentiality of impact over the environment, the use of sugar beet pulp is the most promising alternative. Its reduced environmental loads together with its increased revenues converts this scenario in the more sustainable one. On the other hand, for the corn stover valorization alternative, the large amount of enzymes required for the enzymatic hydrolysis and saccharification process entails a large contribution in the environmental perspective and also no economic profitability is obtained, thus being discarded as an option for nisin production. However, it is important to mention that, from the point of view of the Greenness Grid methodology, a final score of "potentially sustainable" is achieved for the corn stover scenario, whereby the optimization of the process in terms of increased production yield as well as reduced energy requirements can result in providing a viable scenario both economically and environmentally sustainable.

On the other hand, given that these alternatives enable to obtain two products, nisin and lactic acid, a mass and economic allocation has been carried out, in order to determine which of the products have a greater contribution over the economic and environmental scores. From a mass allocation perspective, since the fermentation process leads to produce a higher amount of lactic acid, the impact of this co-product is higher, while as it economic value is lower in comparison to nisin, when performing the economic allocation, the higher contribution is observed for nisin.

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9

Valorization of agricultural and forestry residues for producing nisin

This chapter partially reproduces content already published as "Arias, A., Feijoo, G., Moreira, M. T. (2022). Process modelling and environmental assessment on the valorization of lignocellulosic waste to antimicrobials. *Food and Bioproducts Processing*.".

This research has been supported by iFermenter project (more information on Annex III)

SUMMARY

Energy recovery is the most widespread end-of-life alternative for lignocellulosic waste, but its use as fermentable sugars has been shown to improve sustainability and circularity outcomes. In this context, the valorization of lignin-based residues to obtain bio-products with high added-value in the market value chain appears as a novel and adequate alternative on the roadmap of achieving a sustainable society based on circular economy strategies. Within this framework, the approach of biorefineries as technological schemes for processing integrally renewable resources stands out. Among the different target products, "bioactive" compounds have aroused great interest for their properties and potential characteristics in the food, pharmaceutical and healthcare sectors.

Bearing this in mind, an alternative production scheme has been developed in **Chapter 9**, that evaluates the conceptual design and environmental impacts of the biotechnological production of nisin (co-producing lactic acid) from two waste streams from the agricultural and forestry sectors: olive pruning and eucalyptus residues. The technological feasibility of the alternative process is evaluated by the full-scale modelling using SuperPro Designer software. In addition, an eco-efficiency analysis has been developed to select which feedstock is most suitable as a resource for the production of nisin and lactic acid.

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9.1 Giving a second-life to agricultural and forestry residues

The forestry industry and the agricultural sector are some of the sectors considered strategic to meet the objectives proposed by the United Nations Sustainable Development Goals, specifically those included in SDGs 1, 2, 3, 6, 7, 13, 14 and 15. Regarding the challenges related to climate change, the EU Bioeconomy Strategy and the Climate Change Mitigation Strategy 2050 pursue the promotion of the transformation of sectors towards a circular economy, focused on the use of renewable natural resources. In this area, new markets are opening up for forest resources and products derived from the agricultural sector, with a significant increase on the demand of lignocellulosic bio-based materials.

The integration of biotechnological alternative in those sectors is essential to promote the use and industrialization of bio-based resources, processes that should bear in mind the preservation of the environment and the conservation of the natural patrimony. In this way, an ideal and sustainable coexistence between forestry, agriculture and industrialization might be achieved, while promoting the proper management and conservation of both forestry areas and the primary agricultural sector (Shao et al., 2019).

One of the short-term objectives for the forestry and agricultural sector is to improve competitiveness and innovation from the first stage of transformation, with special emphasis on the later stages, regarding the production and valorization of residues. In this regard, the main advantage of using those waste resources is that it is thought that could provide significant economic benefits, due to its large availability and low price, given its "residual" nature. In addition, the lack of influence over the food chain, as both olive pruning and eucalyptus residues are nonedible materials, converts them in appropriate feedstock for biotechnological production routes (Badgujar and Bhanage, 2018).

Eucalyptus globulus is grown in both Mediterranean and subtropical regions, and its extensive use derives from its rapid growth and high wood density, suitable for the production of paper and board products. In Europe, Spain and Portugal are the most recognized producers, with a cultivated area of more than 1.5 million ha for Spain and 0.8 million ha for Portugal. Given this significant area coverage, the amount of related biomass residues are at least double on a mass basis, estimating a number of 3 million tons for Spain and 1.9 million tons for Portugal, annually. This amount of waste is causing significant management problems and, as mentioned above, burning it is not the most appropriate way to manage it (Lo Giudice et al., 2021). In this regard, its valuable composition on lignin and polysaccharides could entail an advantage for the development of fermentation procedures to obtain bioactive compounds, as assessed in **Chapter 9**.

As for the olive tree, it is the only species of the *Oleaceae* family that provides edible fruit: olives and is ranked as the oldest cultivated tree in the world, whose exploitation has grown rapidly in the last decade. Spain is the main producing region, followed by Turkey, Italy, Greece and Portugal, according to the Eurostat database (**Figure 13**).

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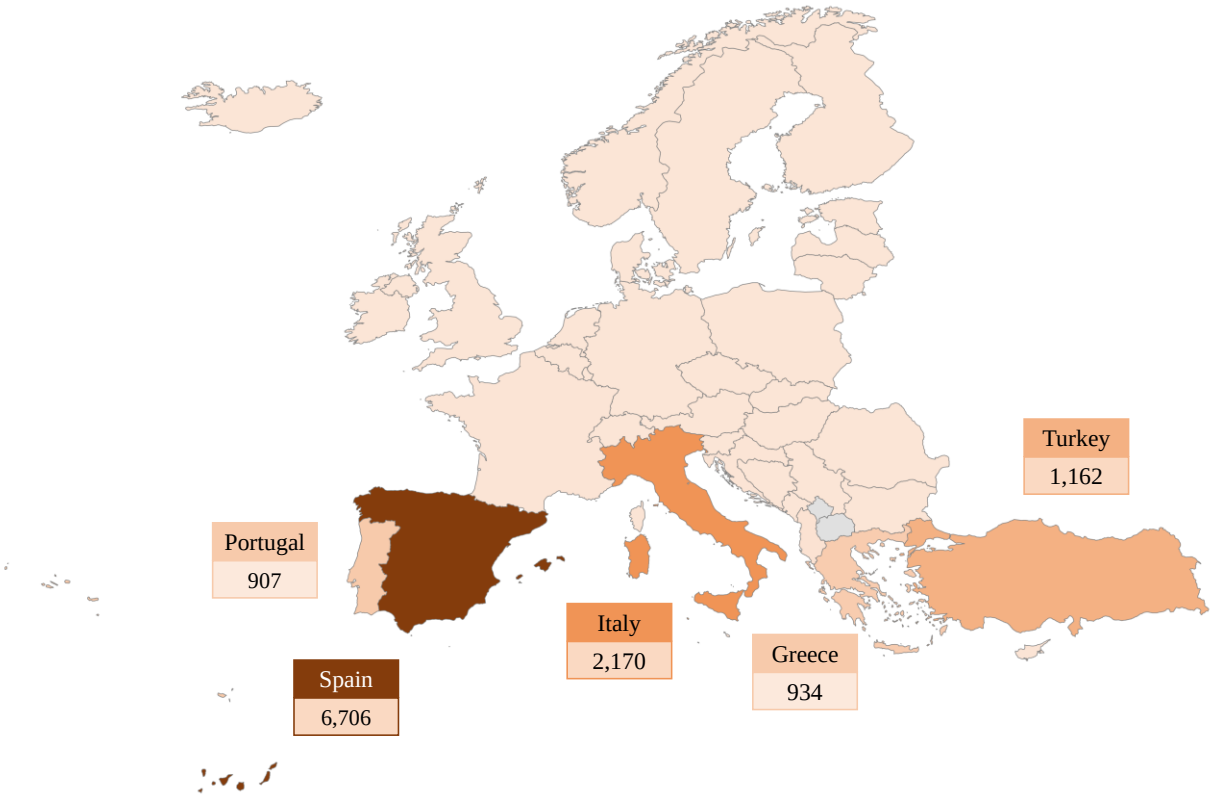

Figure 13. Distribution of olive trees harvesting areas in Europe. Database: Eurostat. Own elaboration.

Some of the environmental burdens identified associated with olive oil production are those related to energy and water consumption, necessary for the agricultural activities of harvesting and cultivation, but also certain gaseous emissions from the use of machinery. However, even so, these impacts are minor compared to those caused by the residues produced during tree pruning, the olive leaves, which, if not properly managed, have the potential to cause significant impacts on soil. The most widespread use of these residues is the production of biomass or animal feed, being, in fact, a "waste of resources", given their outstanding composition in bioactive compounds, which have a high marker value (Espeso et al., 2021).

In this regard, **Chapter 9** presents an alternative way of managing this waste, avoiding other practices that involve environmental impact and inefficiency, i.e. burning, which results in the release of polluting compounds into the environment, in addition to its risk potential, due to the possibility of causing fires, leading to the loss of fertile soil and erosion, the emission of huge amounts of carbon dioxide into the atmosphere, loss of biodiversity and desertification. In addition, non-selective collection would create a negative visual and environmental impact.

With these aspects in mind, an alternative valorisation of the olive pruning and eucalyptus residues is being assessed under an environmental and economic perspectives, considering the production of a high-added value compound, nisin, which properties and characteristics has been previously defined and discussed on **Chapter 8**.

9.2 Process description

The process stages are analogous to that of **Chapter 8** with the pretreatment section being the most different, given the different nature of the feedstocks used (**Figure 14**). To

this end, in **Chapter 9** only the pretreatment section is described in detail, as both fermentation and downstream sections are the same as for SBP and CS feedstocks, bearing in mind that, for the fermentation the equation model 2, depicted on **Section 8.2.3** is used, obtaining the same yield on the release of the available fermentable sugars.

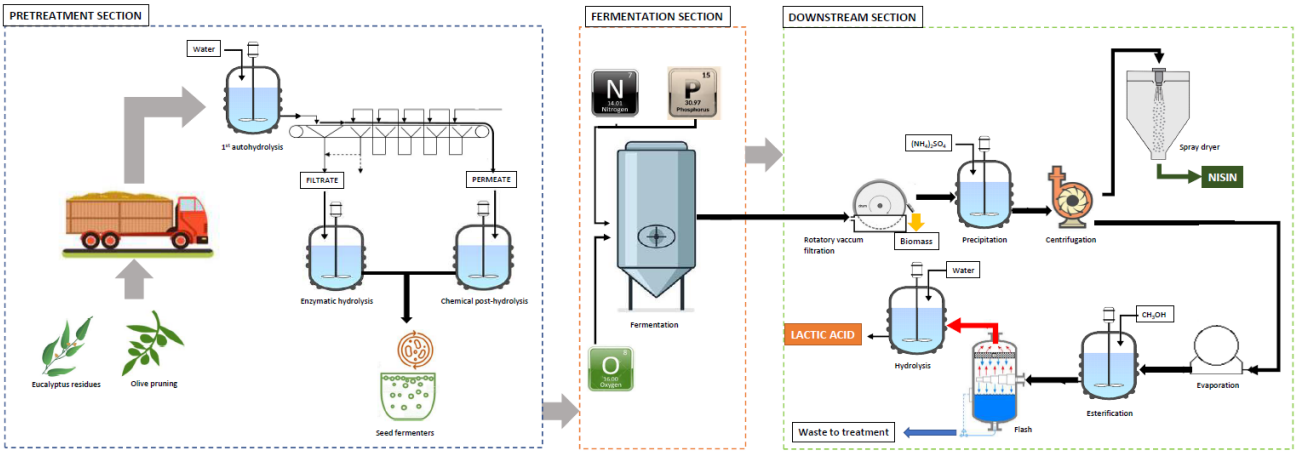

Figure 14. Process diagram of nisin production process with lactic acid recovery using OP (Olive pruning) and ER (Eucalyptus residues) as bio-based feedstocks.

Considering the fermentation stage and the processing capacity of the downstream process, the amount of nisin produced per batch is estimated at 100 kg. Applying the heuristics of the annual operating time of the facility at 330 days/year, the amount of nisin and lactic acid produced in one-year depends on the batch time of each of the production processes developed. The capacity of each production process is shown in **Table 10**, bearing in mind that the batch time corresponds to the time required for the total process, considering the three stages, and the cycle time represents the one required for the fermentation step.

Table 10. Production capacity of the different alternatives studied for nisin production.

Process	OP	ER
Batch time (h)	163	135
Number of batches per year	49	59
Nisin production (kg/year)	8,964	6,579
Lactic acid production (kg/year)	136,279.23	101,016.31

9.2.1 Bio-based feedstock characterization

When considering a biotechnological process based on the valorization of agricultural and related food sector residues, it is important to examine its availability. In the case of olive trees, pruning activities are usually carried out in autumn and winter, extending even into spring but always before flowering. Its most common application is field burning, which causes GHG emissions and soil degradation (Abou Fayssal et al., 2020). The estimated annual production of pruning residue is set at around 1-5 tons/ha of crop (Suardi et al., 2020), especially in Mediterranean regions, which amount to, more or less, a total of 35 Mt of pruning residues per year (Menéndez et al., 2018; Rencoret et al., 2019).

Finally, as for eucalyptus residues, their felling is spread throughout the year, so that forestry operations ensure a continuous flow of residues. Spain and Portugal are the European countries that stand out in the cultivation of eucalyptus, with approximately 1.4 million ha, which implies about 2.8 million tons/year of residues (Nunes et al., 2019).

This variability in collection operations will therefore make it possible to have agricultural waste streams available throughout the annual period and, since the production process is analogous for the three wastes, the adaptation of the process is quite simple to treat them in the same industrial production plant.

From the point of view of the composition of the different waste streams (**Table 11**), the different cellulose and hemicellulose content would make the yields in fermentable sugars different. OP have the lowest content of both hemicellulose and cellulose, so greater amounts of chemicals and energy are required to obtain an equivalent amount of sugars. But, at the same time, it has a lower amount of lignin in its composition, which facilitates pretreatment and molecular decompositions. However, its year-round availability allows the development of a biotechnological process that does not depend on the seasonality of the residue, so that variations in product yield can be offset.

Table 11. Composition in dry weight % of OP and ER. Adapted from: (Barbanera et al., 2015; Mamaní et al., 2022; Silva-Fernandes et al., 2015; Vieira et al., 2021)

	OP	ER
Cellulose	24.5±0.2	36.1±0.6
Hemicellulose	18.8±0.2	23.8±0.3
Lignin	22.2±0.2	26.7±0.3
Ash	3.8±0.1	2.4±0.3
Protein	6.2±0.1	2.8±0.5
Extractives	18.6±0.1	3.6±0.2
Others	5.9±0.0	4.6±0.0

9.2.2 Pretreatment section

The pretreatment section begins with an autohydrolysis stage of the lignocellulosic biomass at 210ºC, which requires high pressure steam and continuous agitation (Silva-Fernandes et al., 2015). Conversion of cellulose around 22% and hemicellulose of 30.9% was considered. After this stage, in a flash evaporation phase, excess water is removed, which can be recirculated to the CSTR to reduce energy requirements and inputs to the autohydrolysis process. The flash output stream is separated into a solid fraction, characterized by its high cellulose content, and a liquid fraction, with a high hemicellulose content.

The solid fraction will undergo an enzymatic hydrolysis based on hydrolases at 50ºC, which allows the conversion of cellulose into glucose with a yield of 93.7%, and of xylose from hemicellulose with a conversion of 38.5%. One of the bottlenecks of the process may be the reaction time required to complete the enzymatic hydrolysis process: 48 h. The liquid fraction will be processed with a chemical post-hydrolysis using sulfuric acid (72% by weight) at 121ºC with a residence time of 1 h. Under these conditions, 97% conversion is achieved in the hydrolysis of cellulose to glucose, and 22% in the hydrolysis of hemicellulose to xylose.

After both sugar conversion processes, a stream rich in fermentable sugars would be obtained, i.e., glucose and xylose, which will be used as carbon sources in the subsequent

fermentation process. Of the total stream obtained, 10% is used for the seed fermenters to produce biomass for the main fermenter, assuming 97% glucose and 95% xylose conversion to yeast.

9.3 Environmental assessment

Process simulation using the SuperPro Designer® tool serves as a strategy to identify the input and output flows of each of the process units and thus compile the inventory data needed to conduct the environmental study of the impacts associated with nisin production. The Life Cycle Assessment (LCA) methodology has been used as a tool to determine the environmental profiles of the different stages of the process.

The functional unit (FU) considered was the production of 1 kg of products in agreement with other studies (González-García et al., 2013; Muñoz et al., 2014; Rumayor et al., 2018). Regarding the system boundaries, a *cradle-to-gate* approach was considered, from the extraction processes to the manufacturing of the final product (Cao, 2017).

The Ecoinvent database has been selected for conducting the life-cycle inventories, as it includes basic information on the main inputs, both materials and energy requirements, and outputs, so that it provides valuable information for the quantification of the environmental assessment of the conceptual designs of the processes proposed in this study (Hesketh, 2017). In this study, Recipe 2016 MidPoint (H) V1.07 World (2010) H/H and Recipe 2016 EndPoint H V1.07 World (2010) H/H. This selection is based on the recommendations of the JRC European Commission for the development of Life Cycle Assessments (European Commission, 2010).

9.3.1 Limitations of the study

Bearing in mind that the production process is proposed based on simulation data, transport activities related to the transport of materials or products have not been considered, since, when a delocalized process is proposed, there are no fixed transport routes associated with the process. Regarding the database, the Ecoinvent® version 3.8 has been used, but for the incorporation of certain chemicals and process inputs, some assumptions has been needed, given the lack of tome of them in the database. For example, KH_2PO_4 was evaluated as KOH, since the molar ratio of phosphorus in both compounds is the same. For NH_4OH added as a nitrogen source in the culture media formulation, NH_4NO_3 was evaluated as an alternative (Ali et al., 2002).

9.3.2 Mass allocation approach

Considering that the production provides two different products that could be valorized, nisin and lactic acid, a mass allocation has been developed. The values considered for each process scenario are depicted in **Table 12**.

Table 12. Mass allocation parameters per product considered for performing allocation procedures.

Scenario	Nisin	Lactic Acid
OP	4.35 %	95.65 %
ER	4.22 %	95.78 %

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9.4 Economic Assessment

In order to evaluate the adequacy of the valorization strategies presented in this chapter, a technoeconomic evaluation has also been developed, taking into account all the related costs associated with the installation: capital costs, operation costs, labor costs, utilities costs and expected revenues, among others. Regarding this last aspect, as previously, it has been considered that the nisin obtained could be sell with a cost of 85€/kg.

The assumptions and considerations for the development of the economic evaluation, the ones considered are analogous to that of the previous chapter: 9 months of construction period, 1 month for start-up, 30 years of project lifetime, 11 months of yearly operation time, 25% of income tax and 3% of interest rate.

9.4.1 Economic allocation approach

Under the economic perspective, also an allocation procedure has been developed, based on the same reason as the one for the mass allocation. The values taken into account for each process scenario are depicted in **Table 13**.

Table 13. Economic allocation parameters per product considered for performing allocation procedures.

Scenario	Nisin	Lactic Acid
OP	97.85 %	2.15%
ER	97.77%	2.23 %

9.5 Environmental results and discussions

In order to assess which feedstock provides a process alternative more suitable from the point of view of an environmental perspective, an analysis of the profiles obtained for each manufacturing process has been carried out, also considering each of the process steps separately. In addition, depending on the identified hot spots, sensitivity and eco-efficiency assessments were conducted to determine the process scenarios that are more environmentally friendly as well as identifying whether the ratios between process productivity and economic profitability fall within an eco-efficient approach.

9.5.1 Scenario I. Olive pruning valorization

The summary of the data used for the modelling of Scenario I on the valorization of olive pruning is included in **Table 14** providing the data used for the subsequent environmental evaluation, including the inputs, outputs and related emissions and waste to treatment.

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Table 14. Main inventory data for the biotechnological valorization of OP residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
OP	0.61	kg	Nisin	42.1	g
Ammonium Hydroxide	76.7	g	Lactic Acid	958	g
Ammonium Sulfate	0.43	kg	*Total*	*1.00*	*kg*
Dipotassium Phosphate	69.7	g			
Enzymes	74.6	g	*Emissions to air*		
Hydrochloric acid	3.55	kg	Carbon dioxide	43.7	g
Methanol	41.5	g	Methanol	0.18	g
Sodium salts	11.4	g			
Sulfuric acid	3.87	g	*Final waste flows*		
Water	1.65	kg	Non-hazardous waste	0.46	kg
Electricity/heat					
Heat	0.50	kg	*Waste to treatment*		
Electricity	7.48	kWh	Wastewater	5.01	L

It has been possible to identify three main hotspots that contribute to the environmental profile of this first stage of the production process (**Figure 15**, upper graph) highlighting the electricity needs, being the main contributor for most of the selected impact categories, with the exception of the FE and ME, for which it is the bio-based feedstock, the olive pruning, the one that entails the highest load. In view of the results obtained in this first stage of the process, the sensitivity analysis should focus on energy optimization, in order to reduce the energy needs of the process. As for the second stage of the process, the distribution of environmental loads shows that electricity needs are the main hot spot and a certain contribution from chemicals is also identified (**Figure 15**, middle graph). The use of phosphate is the one with the highest contribution among the chemicals. Therefore, in this second stage of the process, the optimization analysis should be based on reducing the amount of electricity requirements and the concentration of potassium phosphate considered for the formulation of the culture medium.

Concerning the downstream processing, a more distributed contribution is observed in most of the impact categories, with energy requirements being the main hotspot in the environmental profile (**Figure 15**, below graph). On the other hand, it is also evident that the use of certain chemicals, mainly HCl, entails significant environmental burdens in some impact categories, due to the background activities associated with their production. Focusing on a sensitivity analysis, the optimization of steam use and electricity needs become the key factors to achieve a more environmentally friendly biotechnological process alternative.

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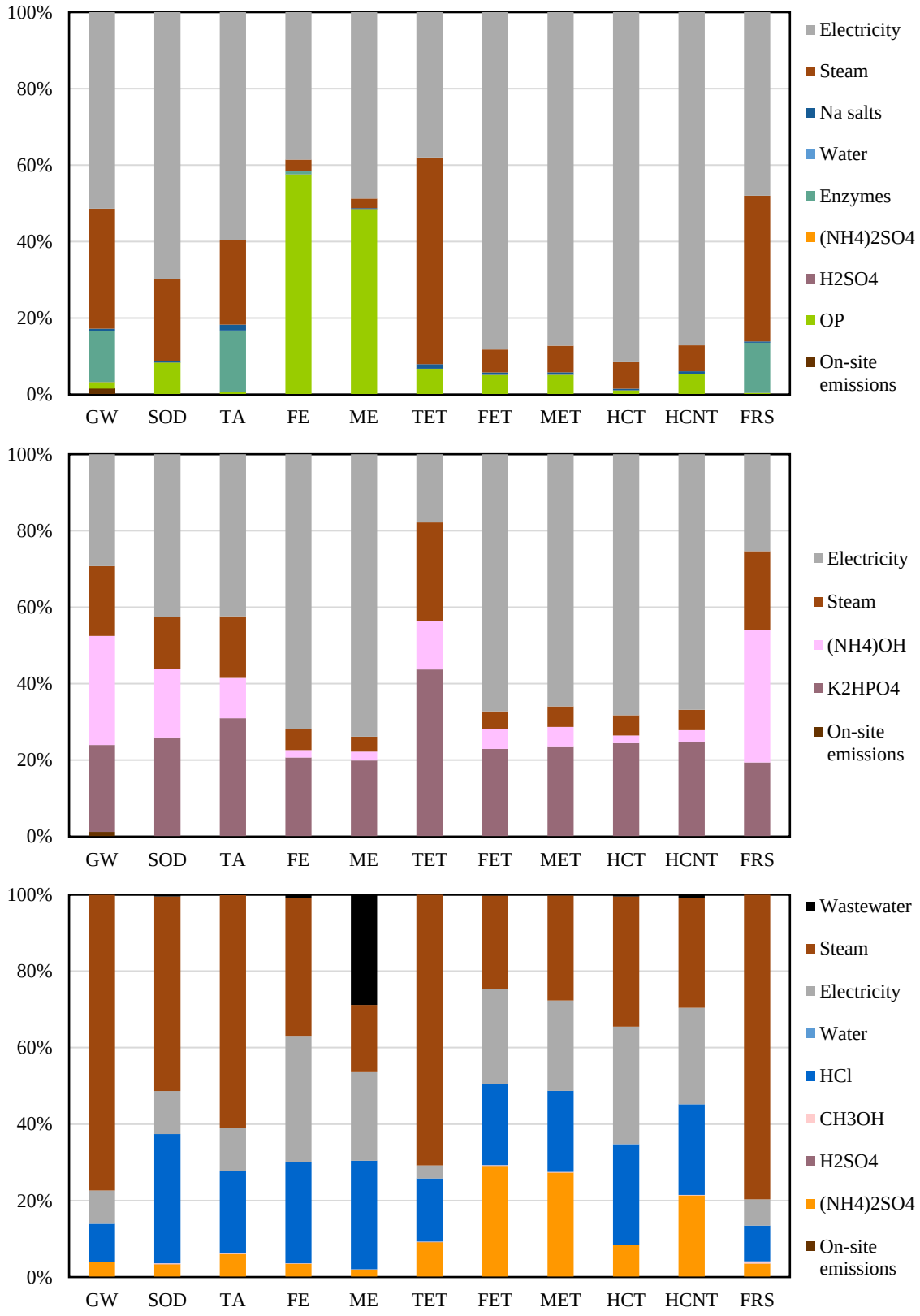

Figure 15. Environmental profile of nisin and lactic acid co-production using OP as substrate. Above (PFS section), middle (FS section) and below (DS section)

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Once each of the environmental profiles of the three sections of the process have been evaluated, it is important to assess which of them represents a greater contribution to the environmental profile of the process as a whole (**Figure 16**). The results show that the fermentation section, which includes the steps necessary for the co-production of nisin and lactic acid, has the highest environmental load on the impact categories of GW, FRS, TET and SOD, and similar to that of pre-fermentation section for the other categories, with the exception of FE and ME. In the case of ME and FE is the PFS the process step that entails the higher environmental impact, the rationale behind this is the impact derived from the use of the olive pruning. Its background activities, the agricultural ones (including cropping, harvesting, fertilization, etc.) leads to a significant contribution over the eutrophication-related categories. Most of this impact is the results of the use of fertilizers, as olive trees requires, in an average value, 4-7 kg of NPK per tree and per year, at least, sometimes required two times the range. In the case of the TET, GW, SOD and FRS categories, the high impact of the fermentation section is the result of the use of potassium phosphate and ammonium hydroxide, whose background production processes entail significant environmental burdens.

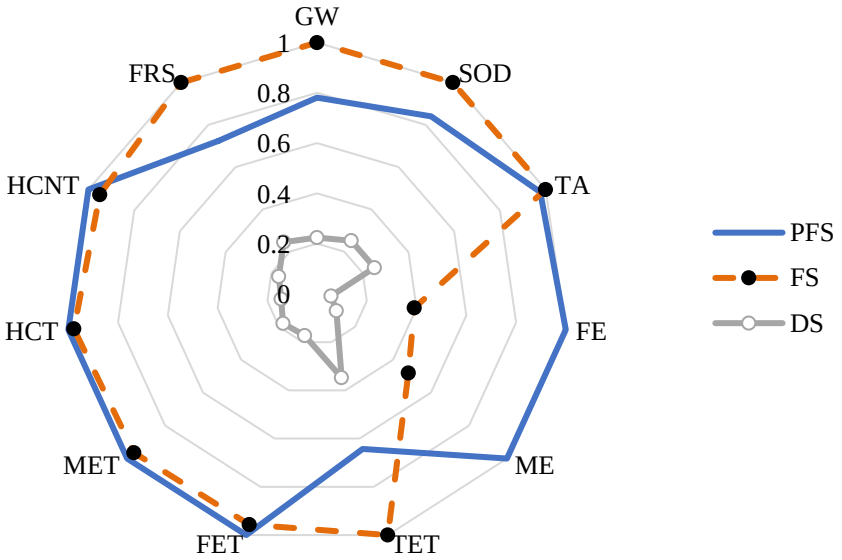

Figure 16. Contribution of the pretreatment (PTS), fermentation (FS) and downstream (DS) sections on the environmental profile of the biotechnological process using OP as the lignocellulosic waste input stream.

In order to provide an improved scenario, a sensitivity analysis is developed, based on the hotspots previously identified. In the case of the pretreatment section, the potential to include actions related to the reduction of electricity needs and the use of renewable energy is endorsed. A “new electricity mix”, is considering, only using renewable resources, mainly coming from hydropower, wind and solar panels. On the other hand, certain impact is observed for the sulfuric acid, so an alternative scenario with reducing 5-10% on this compound requirements is evaluated (**Figure 17**).

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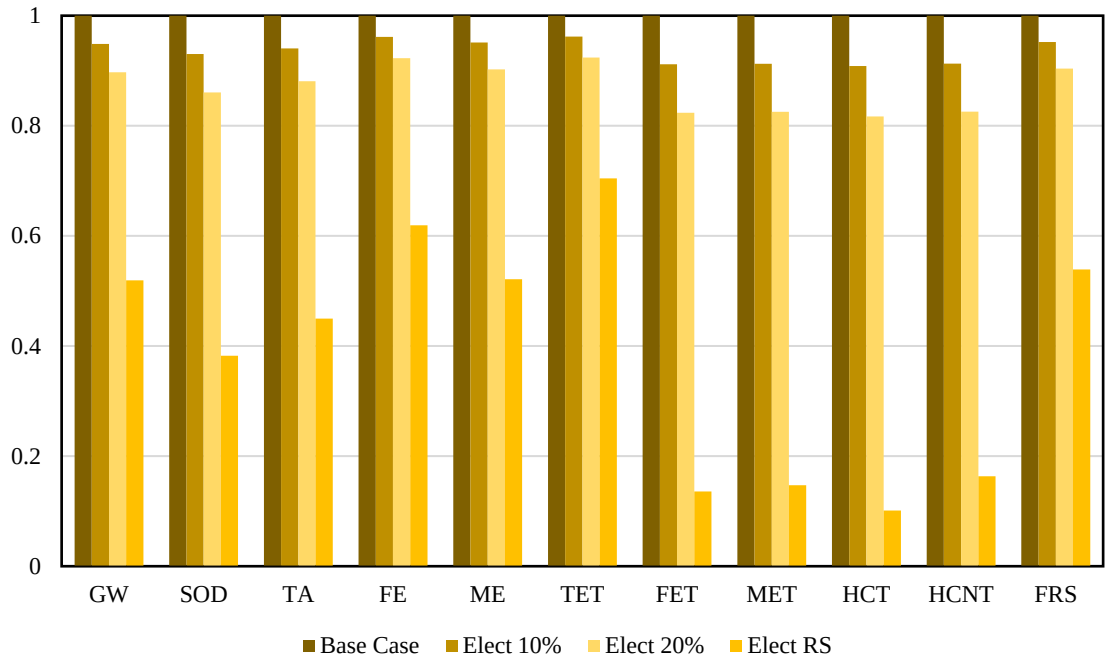

Figure 17. Sensitivity assessment of the environmental profile of the pretreatment section of OP valorisation

The scores obtained by the sensitivity assessment show how the optimization in the use of electricity and the use of renewable resources for its production lead to a significant reduction in environmental impact, the latter alternative being the one that implies a greater reduction. The optimization of the process will allow to achieve values of up to 20% reduction in electricity needs, although the use of renewable energies should be considered as an option with high potential, both from the point of view of environmental impact and sustainability of the process, also including the positive implications it could have on the economic viability of the facility.

For the fermentation stage, the same sensitivity analysis has been assessed for the case of the electricity as the aforementioned one. As another hotspot is observable, related with the use of potassium phosphate, a reduction on the dose of this compound is evaluated, in the range of 5%-10%. It is believed that this decrease in requirements could be achieved by increasing the productivity and efficiency of the process system (**Figure 18**).

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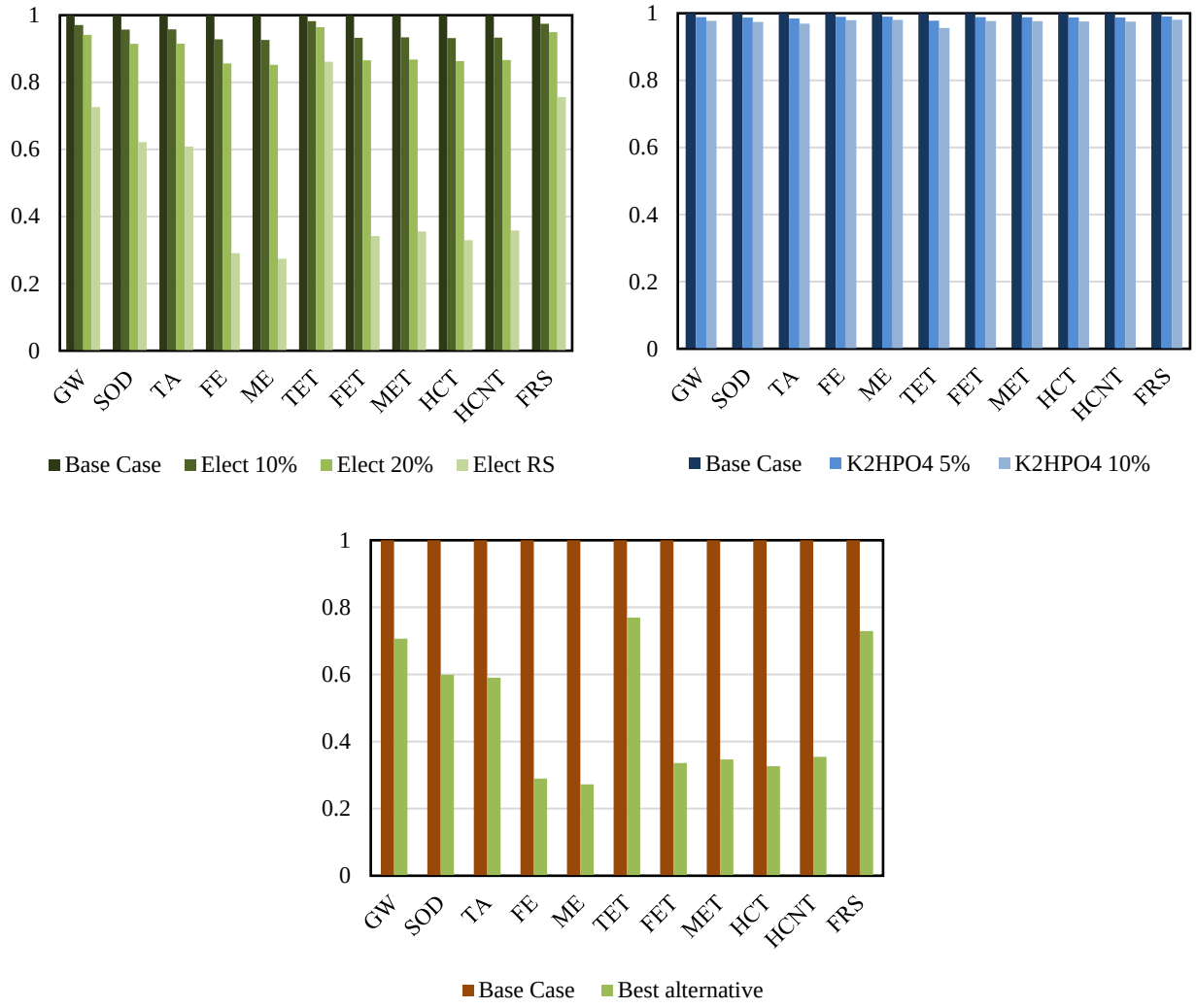

Figure 18. Sensitivity assessment of the environmental profile of the fermentation section of OP valorisation

The values obtained for the optimization of electricity requirements are not as significant as those achieved for the previous sensitivity assessment in some impact categories, such as FRS or GW. The reason is based on the fact that, in those specific categories, the contribution of chemical use on the environmental profile is in most cases as high as that derived from electricity use. But, in fact, the reduced values obtained are significantly higher compared to those achieved by reducing the dose of chemical use. On the other hand, when considering the best scenario provided by the optimization in the use of electricity (the one that considers renewable resources) and by the reduction of the potassium phosphate dosage by 10%, the improvement of the environmental loads is in the range of 23% for the TET impact category and 73% for the ME one. In this sense, it can be concluded that a high degree of improvement of the fermentation stage can be achieved.

Finally, for the downstream stage, steam and HCl are the main hotspots, to this end, the sensitivity assessments are based on (1) 10%-20% steam reduction through energy optimization of the process (2) use of renewable resources to obtain the steam required

and (3) reduction on the dose of HCl in a range of 5-10%. These alternative scenarios are provided in **Figure 19**.

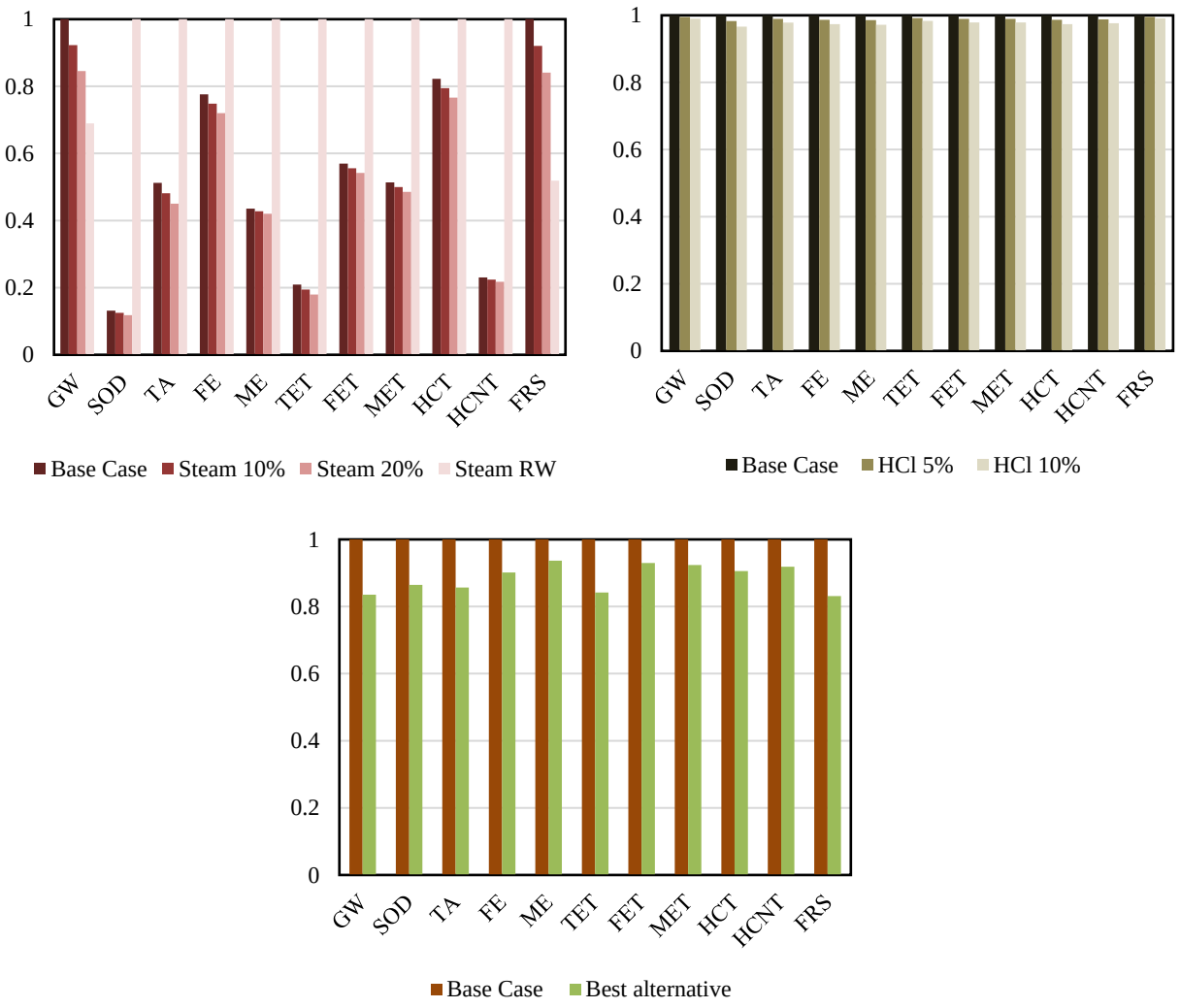

Figure 19. Sensitivity assessment of the environmental profile of the pretreatment section of OP valorisation

As could be observed, the alternative based on the optimization of steam requirements is the one that promotes a better environmental profile, achieving impact loads with a reduction range that amounts to 48% in the case of the FRS category, when an alternative renewable source is used as steam feedstock, and 31% for the GW impact category. However, it should be noted that, although in both impact categories the loads are significantly reduced, the same is not true for the others, as an increase is observed when wood residues are used for steam production. In this sense, it could be concluded that, for this alternative scenario, in general, the optimization of steam requirements throughout the process is the preferred scenario, since reduced environmental loads are obtained, in the range of 2-16%.

On the other hand, as in the previous sensitivity assessment of the fermentation stage, the optimization on the chemical dosage, in this case HCl, is not as significant in

comparison, but still, focusing on chemical optimization should always be one of the main objectives when seeking to improve process productivity, given its contribution to both environmental and economic sustainability.

Finally, by selecting the best scenario provided by the optimization of steam use (the one that considers a 20% reduction in its requirements) and by reducing the HCl dose by 10%, the improvement in environmental loads is in the range of 6% for the ME impact category and 17% for the MRS.

9.5.2 Scenario II. Eucalyptus residues valorization

The summary of the life cycle inventory data used for the modelling of Scenario II on the valorization of eucalyptus residues is included in **Table 15**, considering mass and energy balances, together with the output emissions and waste flows.

Table 15. Main inventory data for the biotechnological valorization of SBP residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
ER	0.65	kg	Nisin	42.0	g
Ammonium Hydroxide	73.0	g	Lactic Acid	958	g
Ammonium Sulfate	0.45	kg	*Total*	*1.00*	*kg*
Dipotassium Phosphate	67.9	g			
Enzymes	39.6	g	*Emissions to air*		
Hydrochloric acid	3.89	kg	Carbon dioxide	30.6	g
Methanol	42.6	g	Methanol	0.17	g
Sodium salts	12.3	g			
Sulfuric acid	5.03	g	*Final waste flows*		
Water	1.97	kg	Non-hazardous waste	0.39	kg
Electricity/heat					
Heat	58.9	kg	*Waste to treatment*		
Electricity	5.27	kWh	Wastewater	5.77	L

Once the life cycle inventory is completed, the SimaPro software and the ReCiPe MidPoint methodology are used to obtain the environmental profile of the eucalyptus residues recovery and valorization processes. **Figure 20** includes the environmental profile of the manufacturing process using ER as a carbon source. As can be seen, the main contributor on the pretreatment (top graph) and fermentation sections (middle graph) are the electricity requirements for most of the impact categories, this contribution being more prominent in the case of the pretreatment section. The seed fermenters are responsible for this important energy demand, in fact, they account for more than 50% of all the energy required for this first section of the production process. In the case of steam, the most prominent contributor in the TET category, it is the chemical post-hydrolysis of the hemicellulose-rich stream that stands out in the consumption of this heat transfer agent, given that the temperature required to favor adequate performance in the chemical hydrolysis operation is 121ºC, thus requiring high pressure steam.

The environmental loads of the fermentation section showed a partial contribution of the chemicals required for the formulation of the fermentation medium with nitrogen, in the form of ammonium hydroxide, and phosphorous, used as dipotassium phosphate **Figure 20**, middle graph). The most significant contribution is observed in the TET category, where ammonium hydroxide represents more than 50% of the impact caused, being the emissions associated with its production process the cause of its high

contribution. Among these emissions, the release of some metallic compounds into the air are the ones that stand out for their impact on the TET category. On the other hand, as with the previous profile, the contribution of electricity needs is also the main hotspot of the process.

On the environmental profile representing the last stage of the process is steam the main responsible of the environmental loads for mostly all the impact categories studied, with the exception of TET and MET, on with the chemical agents needed on the production process also leads to a significant contribution (**Figure 20**, below graph). The drying equipment of this stage is the one that represents a greater demand of heat, being the spray dryer the equipment that entails a greater demand, since it has been modeled to obtain nisin with a high degree of purity, higher than 95% in weight. As mentioned in previous sections, the reason for obtaining this product at such a high degree of purity is based on its possible application in the field of biomedicine and pharmacy, being required to a lesser degree if it is applied as a food preservative, which would significantly reduce the demand for steam in the drying equipment. Therefore, the specification of the type of application of the product would be a fundamental aspect to develop an environmental improvement of the proposed biotechnological process. In addition, the option of performing a higher degree of purification of only a part of the total nisin obtained by the batch process could also be under consideration, thus co-producing nisin of higher and lower purity, with applications for both the food and nutraceutical industries.

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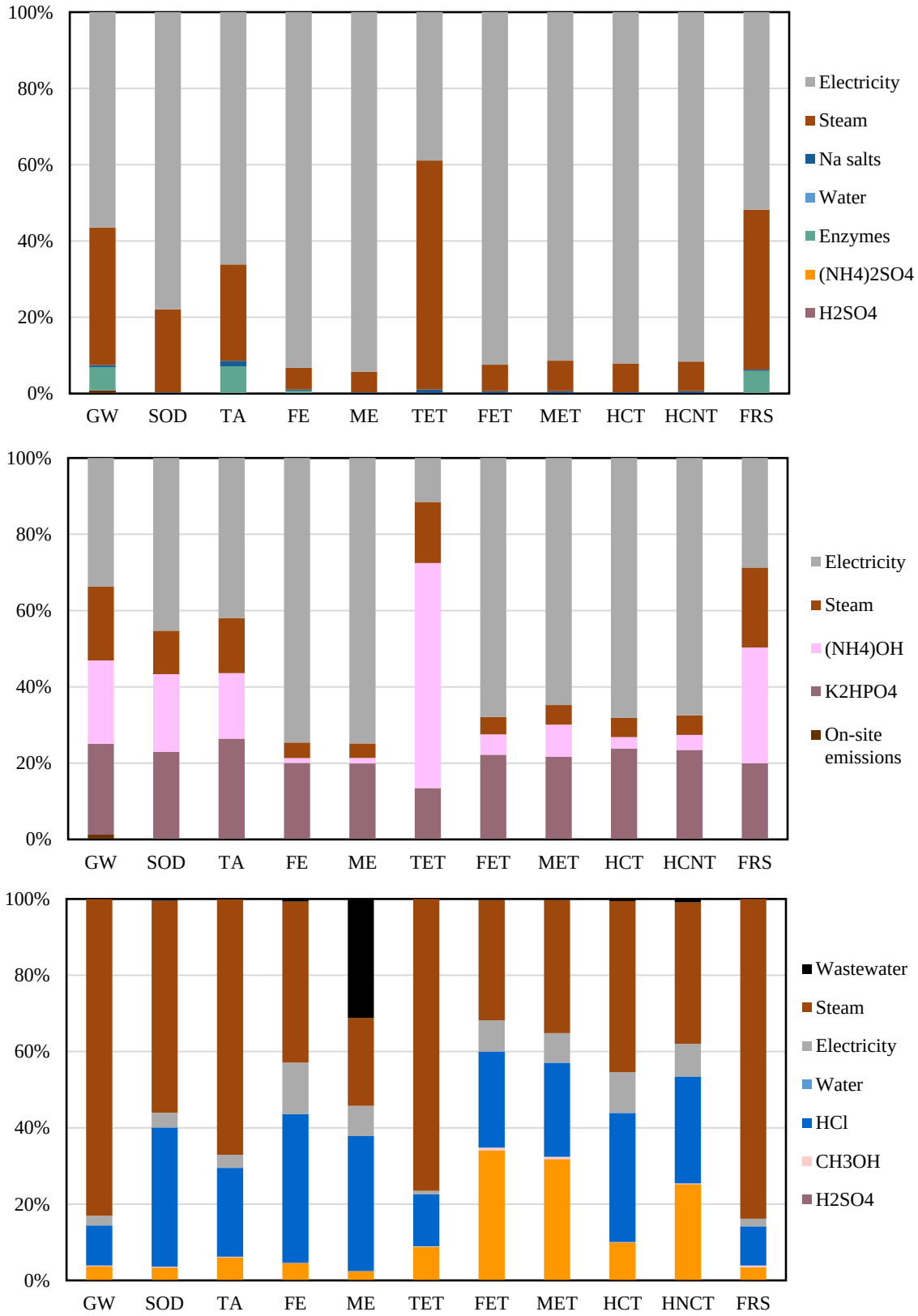

Figure 20. Environmental profile of nisin and lactic acid co-production using ER as substrate. Above (PFS section), middle (FS section) and below (DS section)

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Once each of the environmental profiles of the three sections of the process have been evaluated, it is important to assess which of them represents a greater contribution to the environmental profile of the process as a whole (**Figure 21**). The scores obtained represents that the pretreatment section, which includes all the stages necessary for the release of fermentable sugars and the ones needed for the inoculum in the seed fermenters, has the highest environmental load. Its contribution amounts to a range between 1% for the FRS impact category to 71% for the case of FE when comparing to the impact contribution of the fermentation section. On the other hand, when assessing the differences between the pretreatment and downstream sections, the differences are even higher, with a minimum of 60% of reduced environmental load for the TET category and with a maximum of 97% reduction with respect to the FE one. Besides, there is only one exception to the trend previously explained, as the fermentation section entails an impact 4% higher when comparing to the TET category of pretreatment stage, the rationale behind this the impact derived from the use of the ammonium hydroxide, with a contribution over the profile that end-up with a higher contribution of this stage over the whole process.

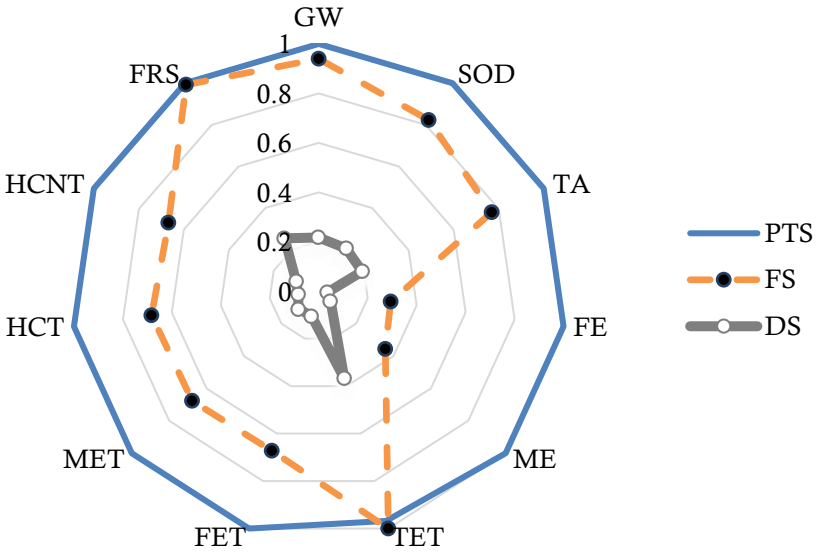

Figure 21. Contribution of the pretreatment (PTS), fermentation (FS) and downstream (DS) sections on the environmental profile of the biotechnological process using ER as the lignocellulosic waste input stream.

In order to provide an improved scenario, a sensitivity analysis is developed, based on the hotspots previously identified. As the electricity is the main hotspot of the pretreatment section, modification on the amount of electricity and steam required and use of renewable resources to produce those energy needs. In this regard, **Figure 22** shows the sensitivity assessment for this first process section.

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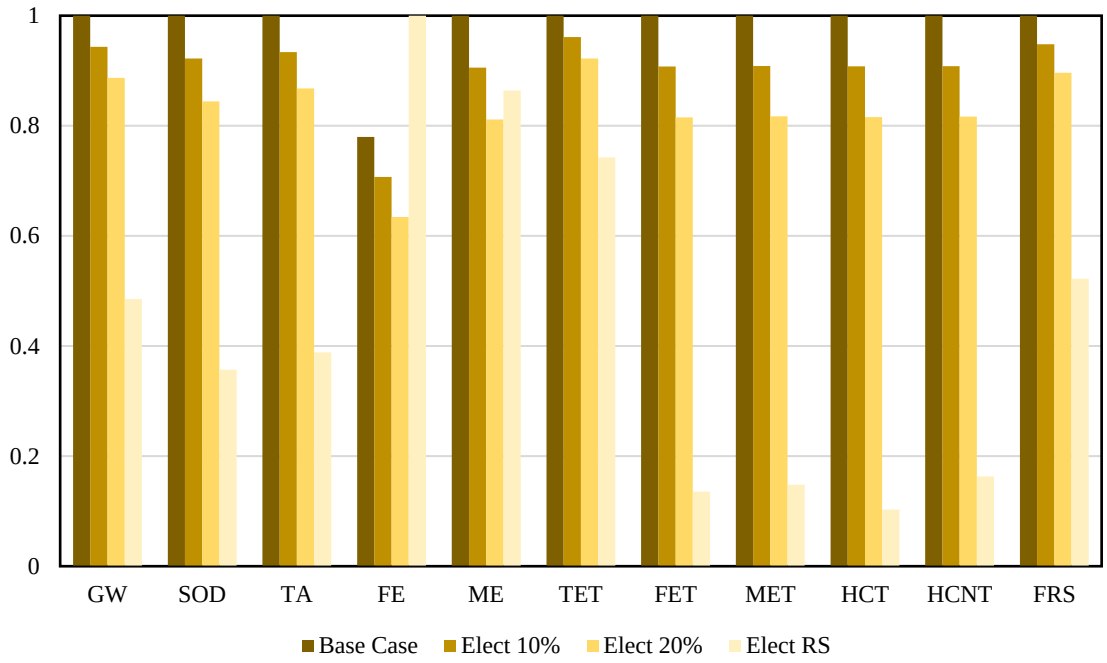

Figure 22. Sensitivity assessment of the environmental profile of the pretreatment section of ER valorisation

The optimization of electricity use implies a significant improvement in all the impact categories evaluated, with the substitution of fossil fuels for electricity generation by the use of renewable resources providing the best environmental profile, with impact reduction values between 14% (for the ME category) and 90% (for the HCNT impact category). The only exception is the FE category, for which the use of renewable resources does not imply an improvement in the scenario, that is, 20% reduction in electricity needs provides the lowest impact.

In the case of the fermentation section, the same approach has been considered for electricity, but in addition, given the enormous impact of the use of ammonium hydroxide for the formulation of the culture medium, a sensitivity analysis has also been carried out to evaluate the impact of its reduction. For this purpose, a reduction in the dosage of this compound, in the range of 5%-10%, is evaluated. It is considered that this reduction in requirements could be achieved by increasing the productivity and efficiency of the process scheme. Taking these aspects into account, **Figure 23** shows the sensitivity evaluation for this first section of the process.

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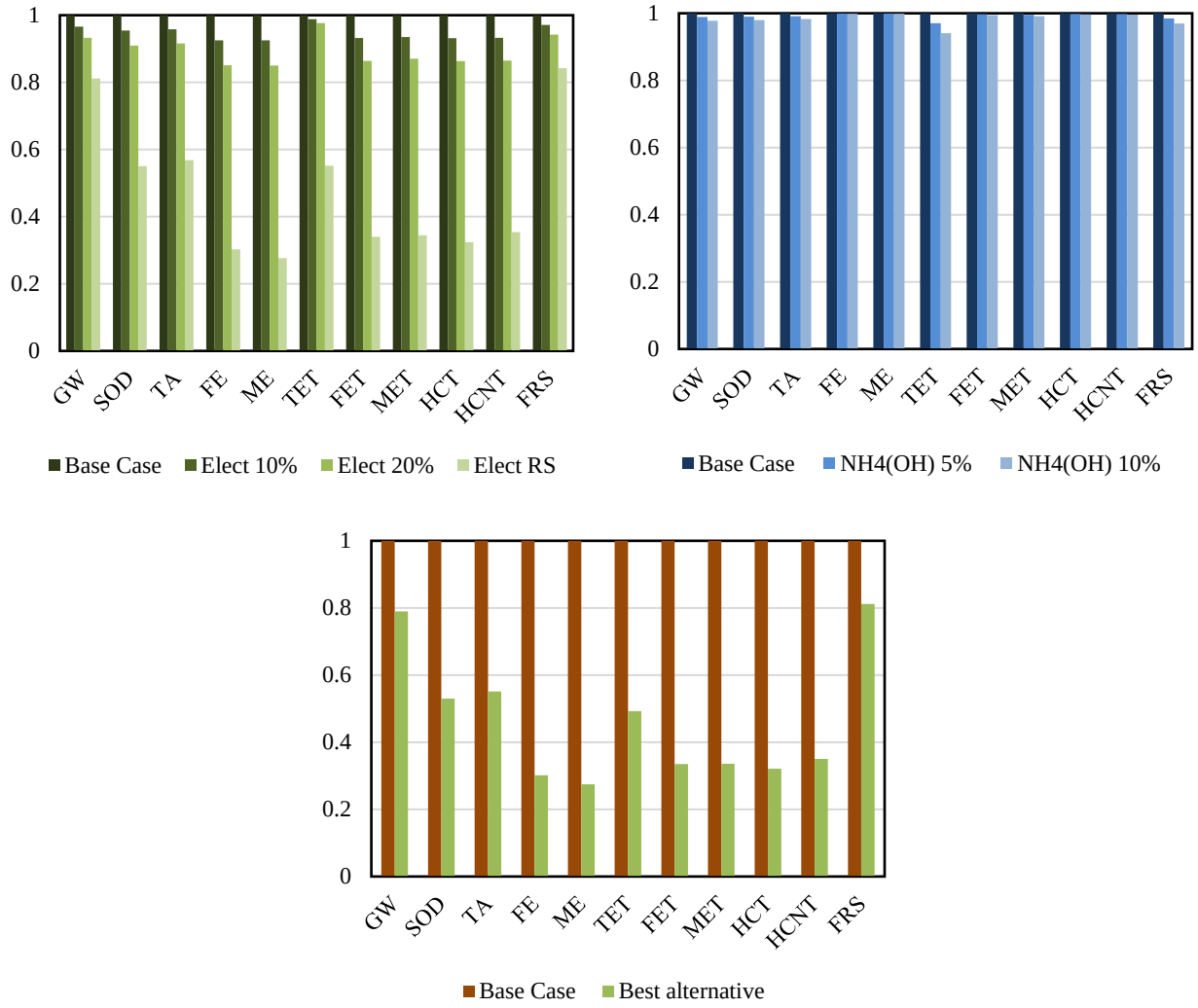

Figure 23. Sensitivity assessment of the ER valorization fermentation section.

As in the previous section, the reduction in electricity requirements implies a significant reduction in environmental loads, ranging from 16% for the FRS impact categories to 72% for ME, when considering the use of renewable resources for electricity production. On the other hand, the reduction in the ammonium hydroxide dose does not provide a significant reduction in environmental loads, the highest achieved is 6% for the TET category, but the other impact categories the improvement in impact is below 3%. Considering the best scenario provided by the optimization in the use of electricity (the one that takes into account renewable resources) and by the reduction of the ammonium hydroxide dose by 10%, the improvement of the environmental loads is in the range of 19% for the FRS impact category and 73% for the ME. In this sense, it can be concluded that a high degree of improvement of the fermentation stage can be achieved.

Finally, in the case of the downstream section, two main approaches could be considered aiming to provide an improved environmental profile: (1) steam requirements reduction by 10%-20%, by the employment of the different temperatures of the process streams that could be used in the heat exchangers units, and (2) use of hardwood residues as renewable resources to be burning for steam production (**Figure 24**). Also, for the downstream section, an analysis on the use variation of the use of HCl is assessed,

considering 5-10% of dose reduction. In this regard, **Figure 24** shows the sensitivity assessment for this first process section.

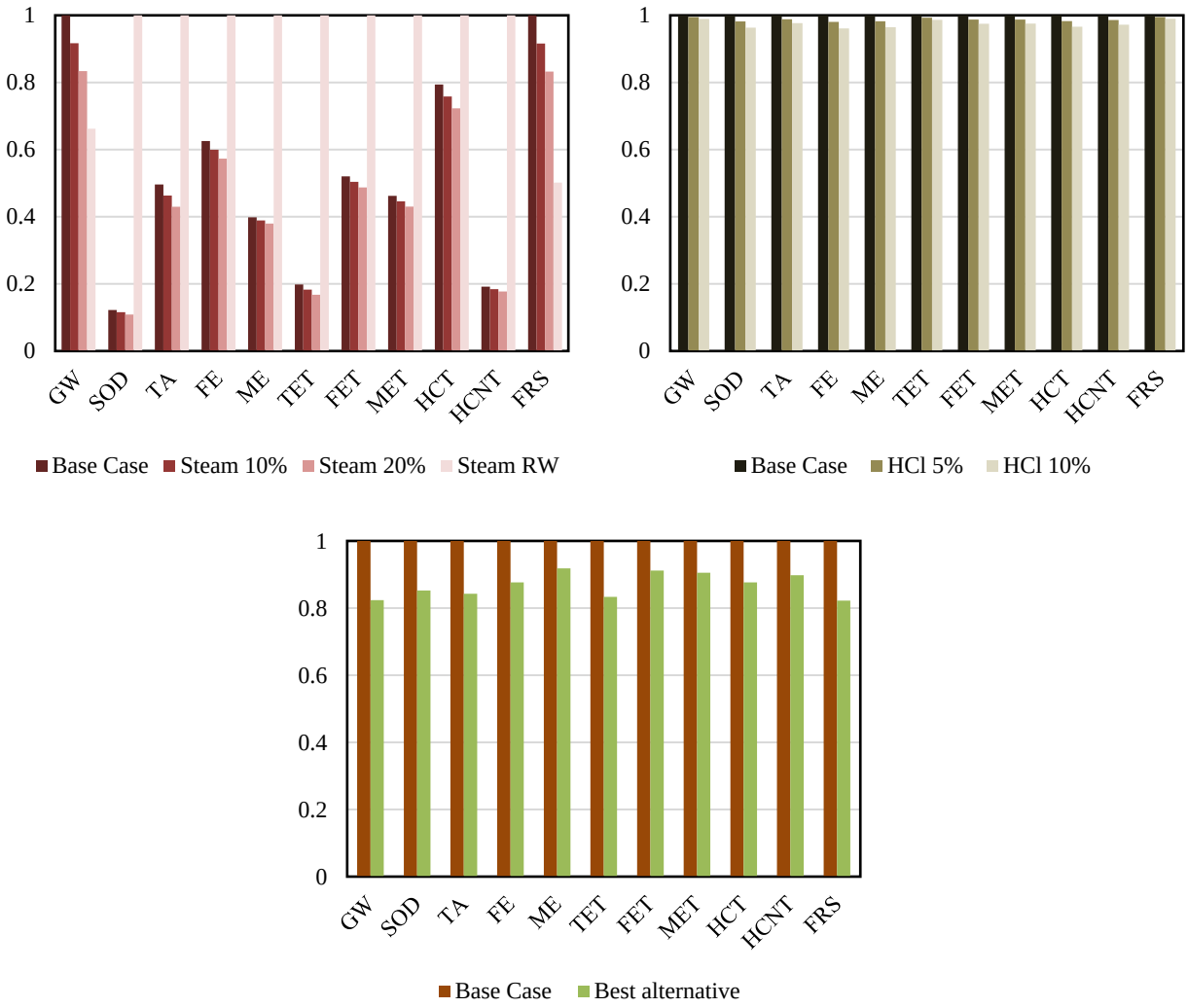

Figure 24. Sensitivity assessment of the ER valorization downstream section.

As can be seen, the optimization of steam requirements is the one that promotes a better environmental profile, reaching values above 80% in the SOD (89%), TET (83%) and HCNT (82%) impact categories compared to the base case, when a 20% reduction in steam use is evaluated. On the other hand, the use of steam from renewable energies, in this case from the combustion of wood waste in a furnace with a capacity of 50 kW, does not imply an improvement in the environmental impact, with the exception of two impact categories: GW, with a reduction of 66% with respect to the base case, and FRS, reaching values with an environmental improvement of 50%. Besides, the reduction of HCl does not provide a significant reduction of the environmental loads, the highest achieved being 4% for the SOD, FE and ME categories, but the other impact categories the improvement on the impact is below 3%.

When considering the best alternative scenarios provided by the optimization in the use of steam (the one that considers a 20% reduction in its requirements) and by the

reduction of HCl by 10%, the improvement of the environmental loads amounts to 18% for the GW and FRS impact categories. Although the range of environmental improvement is not as high as for the fermentation section, the values achieved are significant enough to consider the proposed optimized alternative scenarios.

9.5 Comparison of the damage potential of each alternative

Evaluating the values obtained through the Recipe Endpoint methodology (**Figure 25**), it is concluded that the co-production of nisin and lactic acid that results in the least damage potential is the one that uses OP as a substrate. Another significant aspect of the results obtained is that, according to this methodology, the Human Health (HH) damage category is the most affected. The use of fewer chemicals, efficient energy use and consideration of the option of using renewable energy resources would mean a reduction in the value of the damage obtained for this impact category, reducing in turn the value of the overall damage associated with the processes. Therefore, in order to improve the overall environmental quality of the processes studied, it would be necessary to carry out studies based on the optimization of the production process, as shown in the sensitivity evaluations.

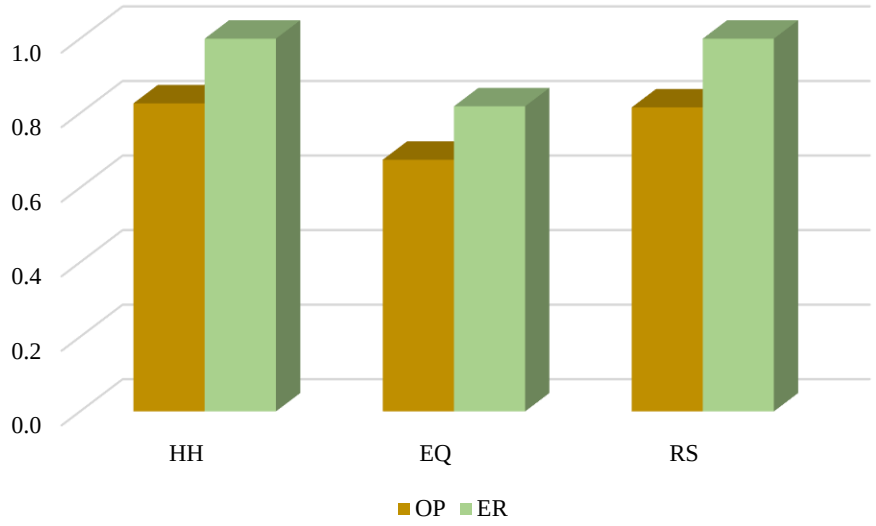

Figure 25. Damage potential values obtained by applying Recipe EndPoint methodology to the proposed alternatives.

9.6 Mass & Economic allocation

The values considered to perform the mass and economic allocation are those included in **Table 16.** As included in the table concerning the production capacities of processes, the amount of lactic acid produced annually is higher than the amount of nisin generated, entailing that when performing the allocation of mass and evaluating the environmental impacts associated with nisin, those are significantly lower than those corresponding to the production of lactic acid. On the other hand, as the market value of nisin, given its wide potential on the food and pharmaceuticals sectors, is much higher compared to that of lactic acid, when evaluating the profile under an economic approach, the contribution of nisin is higher than that of lactic acid (**Table 16**).

Table 16. Mass and economic allocation considering the OP and ER as feedstocks

Olive pruning		MA		EA	
		Nisin	**LA**	**Nisin**	**LA**
GW	kg CO_2 eq	6.73	148.02	151.43	3.33
SOD	kg CFC_{11} eq	$2.31 \cdot 10^{-6}$	$5.09 \cdot 10^{-5}$	$5.21 \cdot 10^{-5}$	$1.14 \cdot 10^{-6}$
TA	kg SO_2 eq	0.02	0.41	0.42	0.01
FE	kg P eq	0.01	0.11	0.12	$2.54 \cdot 10^{-3}$
ME	kg N eq	0.00	0.01	0.01	$1.55 \cdot 10^{-4}$
TET	kg 1.4-DCB	6.58	144.58	147.90	3.25
FET	kg 1.4-DCB	0.09	1.87	1.92	0.04
MET	kg 1.4-DCB	0.12	2.65	2.71	0.06
HCT	kg 1.4-DCB	0.17	3.67	3.75	0.08
HCNT	kg 1.4-DCB	3.95	86.77	88.76	1.95
FRS	kg oil eq	2.05	45.00	46.03	1.01
Eucalyptus residues		MA		EA	
		Nisin	**LA**	**Nisin**	**LA**
GW	kg CO_2 eq	7.84	177.98	181.68	4.14
SOD	kg CFC_{11} eq	$2.78 \cdot 10^{-6}$	$6.31 \cdot 10^{-5}$	$6.44 \cdot 10^{-5}$	$1.47 \cdot 10^{-6}$
TA	kg SO_2 eq	0.02	0.50	0.51	0.01
FE	kg P eq	0.01	0.15	0.15	$3.38 \cdot 10^{-3}$
ME	kg N eq	0.00	0.01	0.01	$2.04 \cdot 10^{-4}$
TET	kg 1.4-DCB	7.89	179.19	182.91	4.17
FET	kg 1.4-DCB	0.10	2.34	2.39	0.05
MET	kg 1.4-DCB	0.15	3.30	3.37	0.08
HCT	kg 1.4-DCB	0.20	4.60	4.69	0.11
HCNT	kg 1.4-DCB	4.78	108.50	110.75	2.53
FRS	kg oil eq	2.39	54.32	55.45	1.26

9.7 Outcomes of the economic assessments.

The economic assessment has been applied to the scenarios of OP and ER. Taking into account all the considerations described for the performance of the economic analysis, the values obtained are shown in **Table 17**.

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Table 17. Economic parameters obtained by performing the economic evaluation of the biotechnological production process of nisin and lactic acid using OP and ER as substrates.

Economic Parameters	OP	ER
Total Investment [€]	6,524,000	7,843,000
Fixed Capital [€]	2,466,000	2,960,000
1. Total Plant Direct Cost [€]	5,303,000	6,383,000
2. Total Plant Indirect Cost [€]	848,000	1,021,000
Labor Cost [€/year]	336,888	355,532
Material Cost [€/year]	470,959	533,797
Utilities Cost [€/year]	142,372	128,773
Annual Operation Cost [€/year]	1,688,000	1,314,000
Revenues [€/year]	2,953,332	2,151,951
1. Nisin [€/year]	761,907	559,187
2. Lactic Acid [€/year]	2,191,424	1,592,764
Gross Profit [€/year]	1,265,000	838,000
Net Profit [€/year]	822,000	544,000
Gross Margin [%]	42.83	38.93
Return on Investment [%]	12.60	6.94
Payback Time [years]	7.93	14.40
Net Present Value [€]	7,681,000	1,957,000

The economic indicators showed that the proposed manufacturing processes are economically viable for both ER and OP substrates, since the Net Present Values (NPV) are positive. Also, the payback time is lower in comparison with the project lifetime, which is also indicative of the profitability of both scenarios.

When comparing OP and ER as feedstocks for nisin production, a main difference is detected, since OP provides a higher production capacity, i.e., a greater amount of nisin and lactic acid obtained annually, which translates into higher economic benefits. In this sense, the higher value of the annual production costs of the OP scenario balanced by the high profits obtained, which converts it in the most profitable option, given that the annual net profits are almost double compared to those obtained using RE.

But even so, both options can be considered economically viable and desirable. In addition, the seasonality of the feedstocks must also be taken into account: while eucalyptus residues can be supplied on a more continuous basis, pruning residues are characteristic of certain times of the year. Therefore, given the analogy between the processes, as well as the feasibility of both, a combination of the feedstocks in the same facility could be considered, which would balance the shortage of supply and, in addition, the variations in the amount of product manufactured from each raw material.

9.8 Eco-efficiency analysis of the alternatives

With the aim of compiling both environmental and economic results, in order to give a final selection of the best scenario, an additional analysis is also included, specifically the eco-efficiency evaluation, based on the 14046 guidelines, by evaluating three indexes related with the economic and environmental pillars, being the costs, profits and

production capacity, the ones embedded on the economic aspect, and the impact loads obtained by the LCA methodology the ones used for the environmental approach. The EEA index values obtained are shown in **Table 18**.

Table 18. EEA indexes obtained for ER and OP scenarios. Acronym EI refers to Environmental Impact.

Index	**€/impact**		**€/ impact**		**kg products / impact**	
Variables	Net profit/EI		Production costs/EI		Production capacity/EI	
	ER	OP	ER	OP	ER	OP
GW	0.04	0.05	0.56	0.40	0.01	0.01
SOD	$1.13 \cdot 10^5$	$1.37 \cdot 10^5$	$1.59 \cdot 10^6$	$1.17 \cdot 10^6$	$1.52 \cdot 10^4$	$1.88 \cdot 10^4$
TA	14.27	16.85	$2.01 \cdot 10^2$	$1.44 \cdot 10^2$	1.92	2.31
FE	49.08	61.60	$6.90 \cdot 10^2$	$5.27 \cdot 10^2$	6.60	8.46
ME	$8.12 \cdot 10^2$	$1.01 \cdot 10^3$	$1.14 \cdot 10^4$	$8.64 \cdot 10^3$	$1.09 \cdot 10^2$	$1.39 \cdot 10^2$
TET	0.04	0.05	0.56	0.41	0.01	0.01
FET	3.04	3.72	42.77	31.79	0.41	0.51
MET	2.15	2.63	30.28	22.52	0.29	0.36
HCT	1.55	1.90	21.76	16.24	0.21	0.26
HCNT	0.07	0.08	0.92	0.69	0.01	0.01
FRS	0.13	0.15	1.84	1.32	0.02	0.02

Within the same approach, on the following figures is depicted the eco-efficiency graphs on the most representative impact categories, considering the net profit against the environmental loads (**Figure 26**), the indexes obtained by the relation between production costs (**Figure 27**) and production capacity (**Figure 28**) in relation with the environmental impacts. The color code is analogous to the previous chapter: eco-efficient (green), non-eco-efficient (red) and intermediate position (yellow).

As discussed above, the ER scenario is the one with the highest environmental loads and the one that produces the least amount of nisin, given its characteristic composition, since a higher percentage of lignin makes its structure less accessible to sugar-based compounds, the "feedstock" used for the subsequent nisin production in the fermentation stage. This fact is translated into a lower net profit, as less amount of marketable product is obtained. Besides, its environmental loads are also higher per functional unit, that is 1 kg of products obtained, which is also expected given its lower production capacity and efficiency in comparison to OP residues.

These facts entail that the eco-efficiency of the base case scenario of ER is not achieved in any impact category, as depicted in **Figure 26**. However, when performing the sensitivity assessment based on the main hotspots of the process, it is observed that the ER production scenario moves from the red to the yellow region, providing a scenario with greater potential to be evaluated as eco-efficient.

On the other hand, for the case of OP production scheme, both base case and optimized scenarios are embedded in the green region, thus being categorized as eco-efficient. Once again, it is demonstrated that process optimization through a more efficient use of energy requirements, as it has been one the main hotspot identified, entails significant improvements under the sustainability approach, both in economic and environmental terms (**Figure 26**).

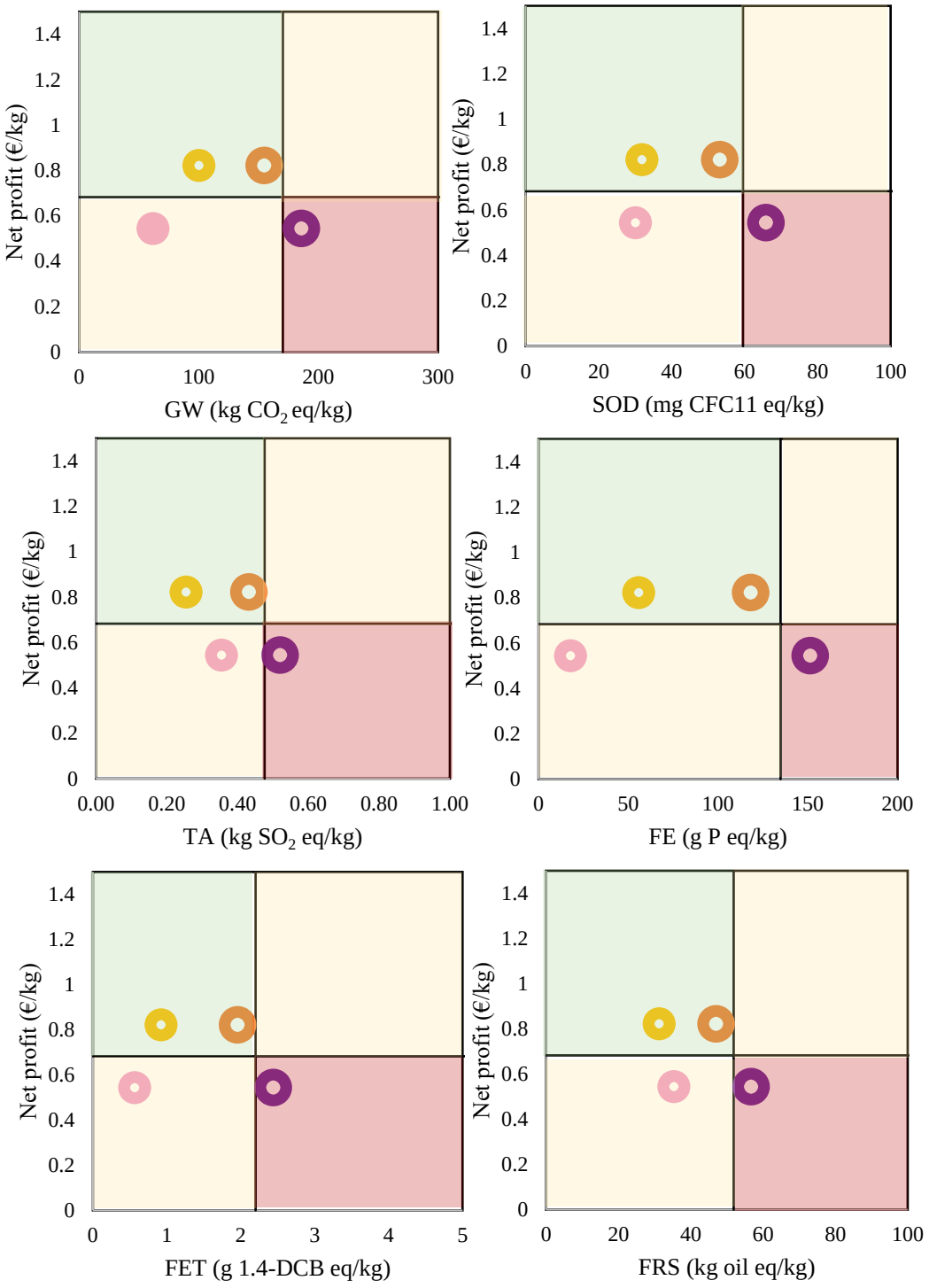

Figure 26. Eco-efficiency analysis considering the index between the net profits of the biotechnological production scheme and the environmental loads. Color code: ● ER base scenario, ● ER optimized scenario, ● OP base scenario, ● OP optimized scenario.

When, instead of evaluating the net benefits of the process, the analysis focuses on the production costs, the difference between the OP and ER scenarios is not so abrupt, since the process scheme and the equipment used are quite similar. However, the fact that the productivity of the process using OP is higher than using ER feedstock, shows again an important contribution to consider them as eco-efficient processes. For all the impact

categories under evaluation the ER base case scenario is categorized as “non-eco-efficient”, but its optimization with the variations on the main hotspots of the environmental profile obtained by the development of the LCA methodology, provides a new ER scenario with the environmental loads sufficiently reduced to be placed on the “yellow region”, that is closer for being catalogued as an eco-efficient process (**Figure 27**). In the case of the OP scenarios, both of them are within the “green quadrant”, thus being eco-efficient in all impact categories, with a better result obtained when the optimized scenario is evaluated since, as with the RE scenario, impacts are considerably reduced, especially in the FET category, followed by GW (**Figure 27**).

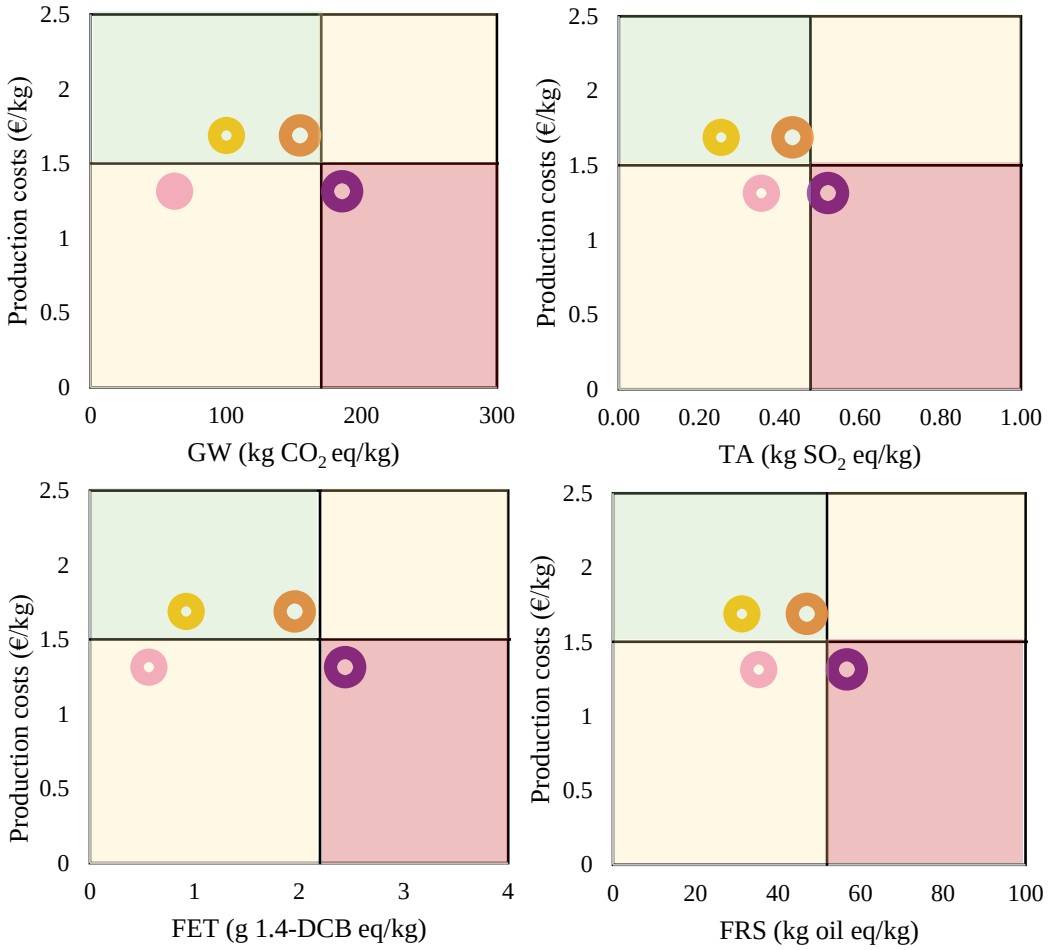

Figure 27. Eco-efficiency analysis considering the index between the production costs of the biotechnological production scheme and the environmental loads. Color code: ● ER base scenario, ● ER optimized scenario, ● OP base scenario, ● OP optimized scenario.

In the index of production capacity versus environmental impact, the trend is similar to that obtained for the index in **Figure 28**, given the implication of sales profits on the net profits of the process. Once again, the OP scenarios, both the base case and the optimized one, are classified as eco-efficient, while the RE-based process is classified as "non-eco-efficient" and its optimized alternative would be in the intermediate zone

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(yellow quadrant). The lower capacity to obtain nisin and lactic acid using RE implies a greater environmental load per unit of product, thus affecting the impacts more.

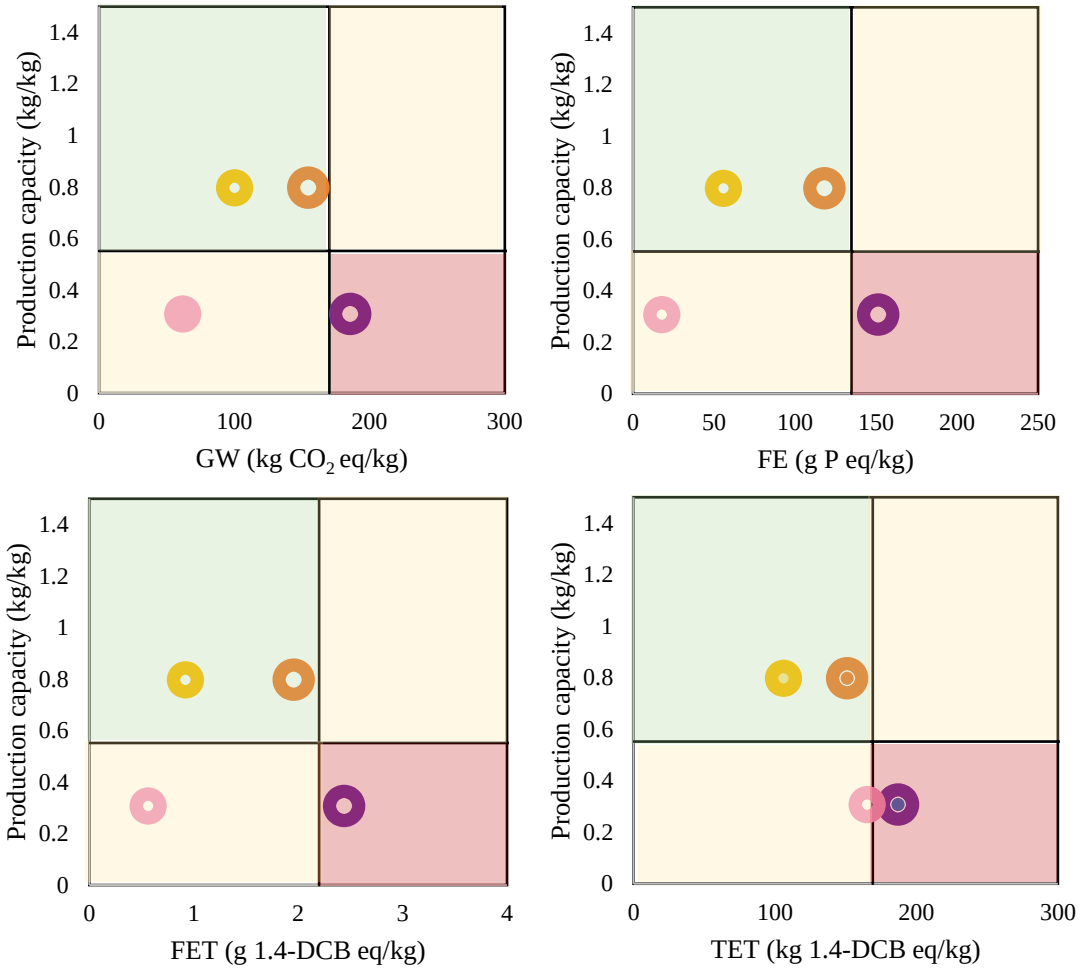

Figure 28. Eco-efficiency analysis considering the index between the production capacity of and the environmental loads. Color code: ● ER base scenario, ● ER optimized scenario, ● OP base scenario, ● OP optimized scenario

9.9 Greenness Grid methodology

The analysis of the effectiveness of the scenarios has also been assessed by the consideration of the Green Chemistry principles, which are evaluated through the scoring of 15 metrics, which are normalized between 0 and 1 in order to obtain de Green Index value, which represents the degree of sustainable potential of the scenarios under evaluation. To this end, **Table 19** includes the main results obtained for the OP and ER process scenarios.

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Table 19. Metric scores values and global Green Index obtained for CW, SBP and CS scenarios**.**

	Metric	OP	ER		Metric	OP	ER
1	E factor	0.89	0.62	**9**	Catalyst	0.00	0.00
2	Atom Economy	1.00	1.00	**10**	Degradability	1.00	1.00
3	Process Safety	0.50	0.50	**11**	Safety	0.98	0.98
4	Reduced Toxicity	1.00	1.00	**12**	Accident Prevention	0.75	0.75
5	Safe Solvents	0.98	0.98	**13**	Carbon Efficiency	1.00	1.00
6	Energy Efficiency	0.30	0.43	**14**	Reaction Efficiency	0.00	0.00
7	Renewable Resources	0.94	0.58	**15**	Mass Productivity	0.95	0.92
8	Avoided Derivatives	0.50	0.50	**GREEN INDEX**		**10.79**	**10.25**

As it could be appreciated, the differences between the OP and ER scenarios as not as significant, being the OP process scheme the ones that achieve a higher green index value, thus considering it as the "best" alternative scenario. As the process equipment and stages are similar between them, not gross differences are detected over the metrics evaluated, with the exception of the metric 6 "Energy efficiency", for which the OP scenario is less efficient in comparison with the ER alternative, as higher environmental loads are related with the energy requirements of the process, and the metric 1 "E factor", which is calculated as the mass of waste produced by kg of product obtained, as higher the ratio as lower the value of the metric. In this case, the OP scheme provides a better use of the residual resources, as lower waste is produced by unit of product obtained. This is related with the increased productivity in comparison to that of ER, for which the process yield of the main stage is lower.

On the other hand, in order to identified which is the degree of improvement needed for each scenario, the **Figure 29** is depicted. Considering that 15 is the maximum score (represented by the green line) to be obtained, the OP scenario requires an improvement of 28.1%, while the ER process schemes need to increase their efficiency by 31.6%.

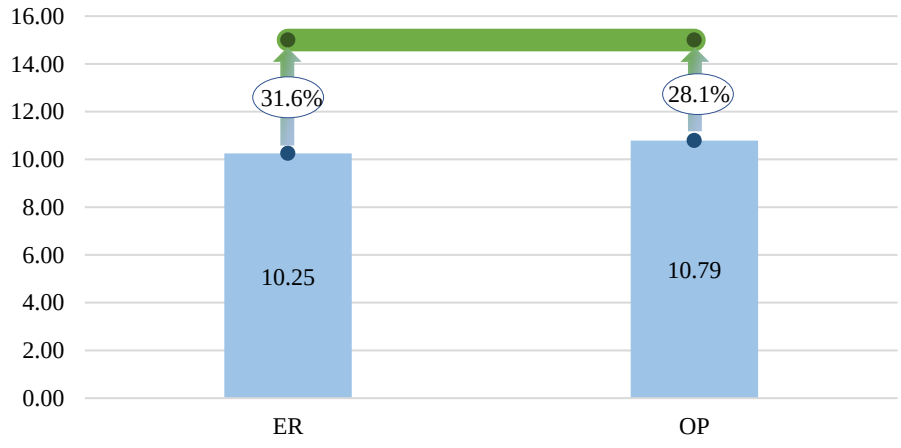

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Figure 29. Green Index score and degree of improvement required for each process scenario for achieve the highest Green Index value.

9.10 Benchmarking between scenarios

As the previous Chapter (**Chapter 8**) has also been based on the production of nisin but using as bio-based feedstock agri-food related food wastes, it is included a comparison between the scores obtained by each process alternative, considering both environmental and economic assessments. **Figure 30** and **Figure 31** include the comparison regarding the environmental point of view, considering both base case and optimized scenarios, respectively. On the other hand, is based on the economic approach. In this regard, it is possible to select "the best" feedstock to be used on the production of nisin and lactic acid.

Regarding the comparisons between the base scenarios, without optimization, the use of corn stover (CS) is the one that results in a greater environmental impact in most of the impact categories under study, with the exception of 5: GW, FE, MET, HCT and FRS, where the use of waste streams with a higher lignin content, i.e. OP and ER, leads to a greater environmental load, ER being the highest in the above mentioned (**Figure 30**).

The scenario with the best projection would be SBP, followed by CW. Its sugar content, as well as its pretreatment processes, which is where the greatest difference with respect to the other scenarios is observed, is the main key to obtaining greater process productivity and, therefore, a lower associated impact. It is only noted that, in the case of CW, the environmental damage on the FRS category is slightly higher than that of CS, given the steam requirements, which amount to 383 kg/FU, higher than those required for the SBP and CS scenarios, 158 kg/FU and 124 kg/FU, respectively.

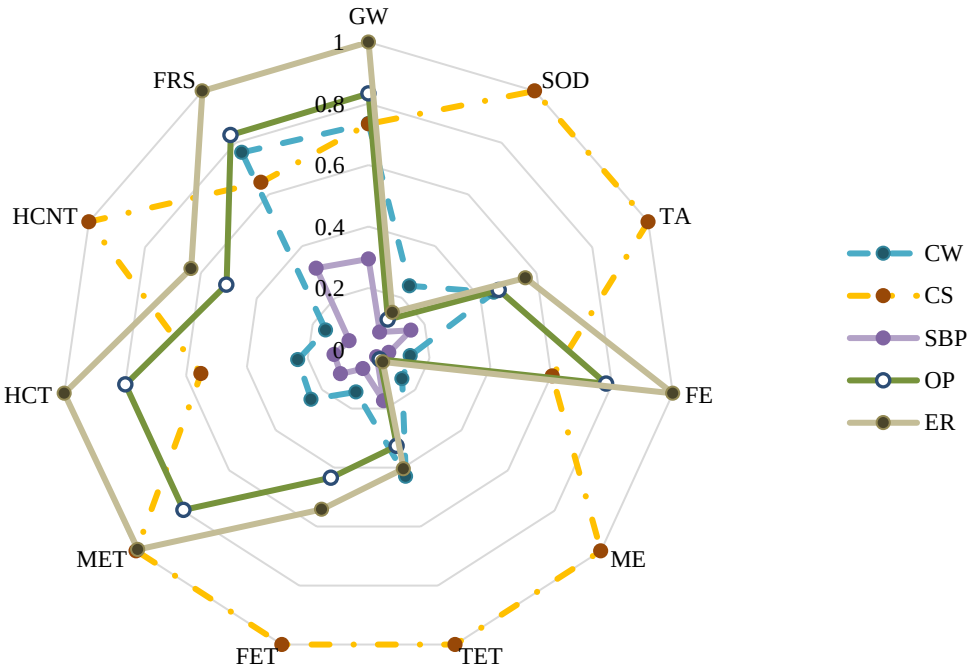

Figure 30. Benchmarking between agri-food and forestry-based residues base case scenarios. Acronyms: CW (Cheese Whey), CS (Corn Stover), SBP (Sugar Beet Pulp), OP (Olive Pruning) and ER (Eucalyptus residues)

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The optimization of the scenarios, through the development of sensitivity analysis around the variables that contribute most significantly to the environmental profile, causes some variation in the ranking of the scenarios in terms of their associated environmental impacts. In this case, the OP and ER scenarios are no longer the most impacting, with the CS scenario becoming the worst for all categories except for one, the FE, where the use of ER contributes most significantly to the environmental load (**Figure 31**).

Regarding the lower impact scenarios, the trend is analogous to the previous case, with the SBP being the best (**Figure 31**). In the case of CW in some impact categories, such as GW, SOD, TA, TET and FRS, even when optimized, it reaches higher values compared to the ER scenario. Therefore, in this case, a compromise solution would have to be reached when selecting the second most "environmentally suitable" scenario. Therefore, given the results of the base case, as well as being able to generate product with a higher degree of efficiency, the CW scenario is considered to be more efficient and suitable.

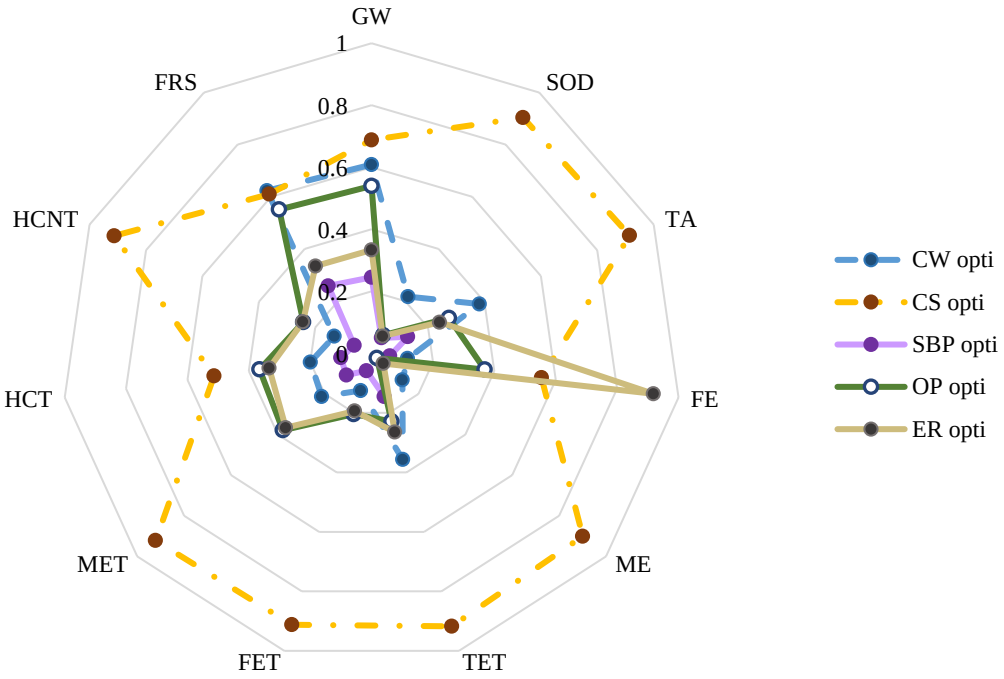

Figure 31. Benchmarking between agri-food and forestry-based residues optimized scenarios. Acronyms: CW (Cheese Whey), CS (Corn Stover), SBP (Sugar Beet Pulp), OP (Olive Pruning) and ER (Eucalyptus residues)

Figure 32 is also included with the comparison between net benefits, production costs and facility capacity. Two scenarios are observed that stand out above the average, the SBP, with a greater productive capacity and net profit, but also with the highest production costs, and the CW, where it is observed that the difference in production costs and benefits is higher, given the lower productive capacity when compared to the SBP. To this end, it can be considered that both processes are efficient from the economic point of view, contrary to the case of CS, where the ability to generate profit is not enough to offset the costs associated with the process, thus being an economically non-viable production model. Regarding the ER and OP scenarios, beyond the fact that a significant decrease is observed compared to the agri-food base scenarios, it is important to mention

that both are economically viable processes and that, even when their capacity is lower, the commitment to its use as a source of fermentable sugars should be considered effective and adequate under a techno-economic perspective.

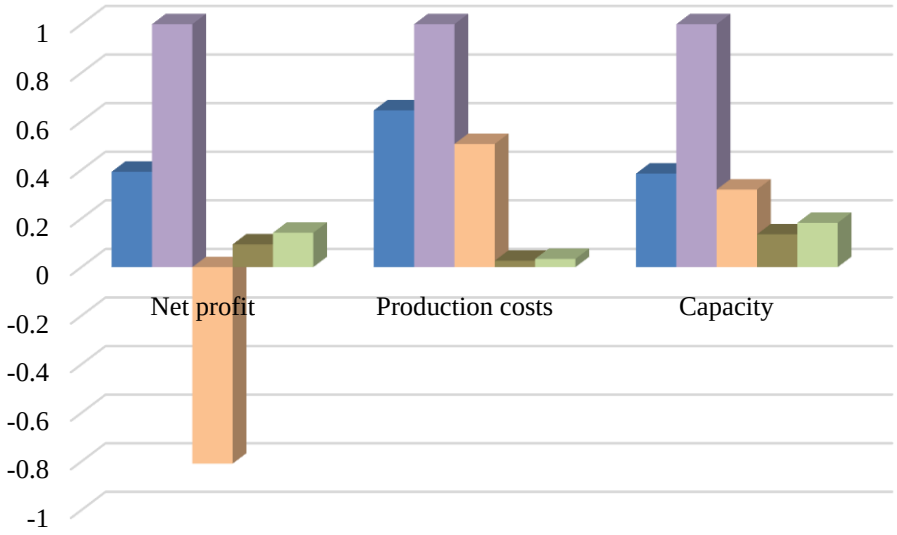

Figure 32. Economic benchmarking between agri-food and forestry-based residues base case scenarios. Color code: Blue (Cheese Whey), purple (Sugar Beet Pulp), orange (Corn Stover), dark green (Eucalyptus residues) and light green (Olive Pruning).

Besides, as the Greenness grid methodology has also been used to evaluate the scenarios, a comparison between the scores obtained is also provided in this section (**Figure 33**). As can be seen, in line with the above discussion, the SBP scenario is the most efficient also from the point of view of green chemistry principles, followed by OP and CW. This is mainly due to the efficiency in the use of energy resources and the productivity of the process.

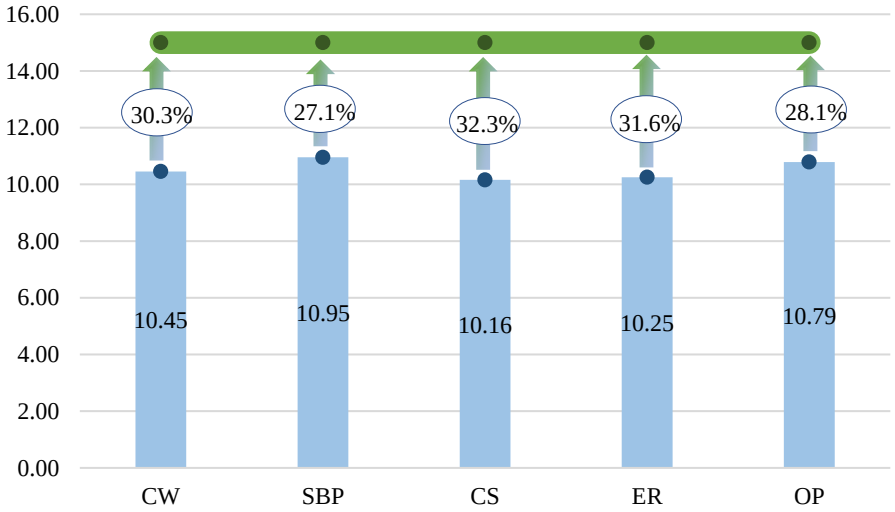

Figure 33. Economic benchmarking between agri-food and forestry-based residues base case scenarios. Color code: Blue (Cheese Whey), purple (Sugar Beet Pulp), orange (Corn Stover), dark green (Eucalyptus residues) and light green (Olive Pruning).

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9.11 Conclusions

In this chapter, a biotechnological procedure of nisin production using eucalyptus residues and olive pruning has been developed. One of the main drawbacks detected for this valorization scenario is the need of an intensive pretreatment for the release of the fermentable sugars, that are subsequently used in the fermentation media as carbon source, which implies a high contribution over the environmental profile obtained, given the huge demand on energy requirements. Regarding the production capacity, it is considered as adequate, as both alternatives are feasible from an economic perspective, thus increasing the potentiality of the valorization scheme proposed for these residues. On the other hand, when comparing both scenarios under an environmental perspective, no significant differences are observed between them, being eucalyptus residues scenario the one with the slightly higher environmental loads.

Even the good results from the economic perspective and from the development of the Greenness Grid methodology, which considered both scenarios as "potentially sustainable", when evaluating the alternatives through the eco-efficiency analysis, none of them reaches an "eco-efficient" value for the base case studies, although when the optimization of the alternatives is assessed, mainly based on the reduction of energy demand or the use of renewable resources, this eco-efficiency value is reached. Therefore, future research should focus on energy optimization of the production process in order to achieve a higher degree of sustainability.

Lastly, when comparing the scenarios studied on this chapter with the previous ones of **Chapter 8**, it has been concluded that, even though all of them are promising sustainable scenarios under the principles of Green Chemistry, the valorization of sugar beet pulp and cheese whey seems to be more adequate renewable resources, given the reduced environmental loads and the increased economic benefits.

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SECTION V
Active biofilms

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SUMMARY

The ever-growing global demand for plastics, coupled with the environmental concerns related with the use of fossil-based resources has resulted in the exploration of alternative sources and sustainable production methods. In this context, biobased plastics have emerged as a promising solution, offering both environmental benefits and potential for circular economy practices. In this **Section V** the main focus is the production and assessment of a biobased active film derived from the recovery of a residual feedstock coming from agrifood sector. By the opting for the use of renewable resources to produce biofilms, it is expected a reduction on the reliance on fossil fuels and a promotion of waste-to-value strategies. Besides, by developing this strategy of valorization, not only a reduction on waste generation is achieved, but also it is expected to aid on the mitigation of the environmental burdens associated with plastic production. To this end, the bio-based production alternative could be considered to be in line with the principles of sustainability and circular economy.

Therefore, this **Section V** of the thesis includes two chapters, both focused on biobased films for food preservation, while of **Chapter 10** a biotechnological production route of a polylactic acid active biofilm is developed, by using wheat straw as feedstock, on **Chapter 11** a multicriteria roadmap for the analysis of an early stage of design food packaging film prototype is proposed, considering both sustainability and circularity criteria.

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10

PLA bio-polymer and nisin: an active food bio-film

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SUMMARY

The new consumption patterns based on the "use and throw away" trend has led to an increase in the production of petroleum-based plastics for their application as food packaging films, leading to significant environmental impacts. In the search for alternatives to conventional plastics, polylactic acid (PLA) stands out due to its renewable origin, its mechanical properties and its biodegradability potential.

To this end, this "**Chapter 10. Biorefinery approach for the co-production of PLA biopolymer and nisin, used to obtain an active food biofilm**" addresses the large-scale simulation of a bio-technological process for the valorization of wheat straw residues for the co-production of nisin and lactic acid through a batch-type fermentation process. Subsequently, lactic acid will be used for the production of PLA films, to which nisin will be applied to provide functional antimicrobial films. To assess the degree of environmental impacts and sustainability of this biotechnological process, Life Cycle Assessment, considering a cradle-to-gate approach, and Greenness Grid methodologies have been applied.

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10.1 Introduction

In response to the consumption habits of today's society, the agri-food industry has progressively implemented production and preservation technologies that guarantee the hygienic quality of food (Brandão et al., 2021; Gutiérrez, 2019) towards the use of biodegradable packaging systems that displace the massive use of plastic (Al-Tayyar et al., 2020; Gopalakrishnan et al., 2021; Kouhi et al., 2020). According to data from the European Bioplastics Association, the global production capacity of bioplastics will increase from around 2.11 million tonnes in 2020 to approximately 2.87 million tonnes in 2025. Among the different types of biopolymers, the group of biodegradable plastics, including PLA (Poly lactic acid), PHA (polyhydroxy alkanoate), starch blends and others, represent the largest share with almost 60% (more than 1.2 million tonnes) of the global bioplastics production, which will facilitate the supply of raw material for various industrial sectors and the possibility of lowering their price.

The ability to be biodegradable, compostable, low-cost manufacturing and environmentally friendly have made PLA biofilms good candidates for the development of food packaging films. However, certain reinforcement strategies need to be considered when it comes to using such biofilms as food packaging materials. Barrier properties, i.e., water and heat resistance, need to be improved to ensure proper food preservation. However, there are studies that address the development of techniques that, in a simple way, can significantly improve these weaknesses, without forgetting the "bio/natural" concept. For example, the addition of bio-nanocomposite materials in biofilm shows that water resistance can be increased by 60% (El Bourakadi et al., 2021; Hong et al., 2021; Ivankovic et al., 2017).

Beyond the traditional "packaging" approach, new food preservation technologies are emerging under the umbrella of "active packaging" (Akhter et al., 2019; Chen et al., 2021; Monjazeb Marvdashti et al., 2019). These are systems designed to intentionally incorporate components that either release beneficial substances such as antimicrobials, antioxidants, flavorings, or absorb substances from the packaged food or its environment such as unwanted or harmful substances such as oxygen, moisture or unpleasant odors. Through the technological development of active packaging systems, it is possible to correct the shortcomings of traditional preservation technologies for packaged foods, improving their quality, extending their shelf life and avoiding food waste (El Bourakadi et al., 2021; Hong et al., 2021).

In addition to the potential of bioplastics as a food packaging material, there is a renewed interest in fresh and "natural" products, i.e., products without artificial additives and preservatives that retain their nutritional and organoleptic properties after processing. Beyond thermal processes and chemical additives, bacteriocins emerge as potent antimicrobial agents and offer the possibility of preserving foods and especially their organoleptic quality. In fact, several research articles have evaluated the use of nisin for the production of functional food packaging materials, reaching its efficacy against foodborne pathogens (Jin and Zhang, 2008; Mauriello et al., 2005). In particular, nisin stands out not only as a natural bio-preservative but also in the biomedical and pharmaceutical field as it reduces the undesirable effects of certain antibiotics and is effective in the treatment of infections related to drug-resistant, gastrointestinal and respiratory pathogens, among others (Ellis, 2018; Shin et al., 2016). As an example of cutting-edge research, the inclusion of bacteriocins in nanomaterials has shown positive preliminary results as a potential anti-cancer treatment, reducing the growth of tumor cells (Naskar and Kim, 2021).

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10.2 Description of the bio-technological biofilm production

In order to evaluate the environmental profile associated with PLA-based active packaging, the production process has been divided into four sub-systems: SS1. Pre-treatment, SS2. Fermentation, SS3. PLA film production, comprising 4 main stages: Oligomerization (SS3.1), Pre-polymerization (SS3.2), Polymerization (SS3.3) and Purification (SS3.4), and finally the subsystem SS4. Active production of packaging film.

10.2.1 SS1. Pre-treatment

According to a recent study addressing the development of a linear regression model to estimate the generation of post-harvest wheat residues, it is concluded that a total of 58.3 million tonnes of wheat crop residues will be produced in the European Union in 2030, a value that shows the wide availability of this resource for use beyond its use on farms as fodder, animal bedding or as amendment for compost (Hỳsková et al., 2020). Thus, the biotechnological valorization process of this bio-based residual steam is considered as a viable alternative for plastic-based food packaging.

In this regard, the first stage for the valorization of wheat straw residues starts with a pre-treatment to promote the release of sugars present in the molecular structure of the lignocellulosic biomass (**Figure 1**). Wheat straw is characterized by a high content of cellulose (28-39%) and hemicellulose (23-24%) (Tufail et al., 2021), which makes it an excellent source of fermentable sugars.

The SS1 subsystem starts with an autohydrolysis stage at high temperature, 210ºC, and high pressure, leading to the release of fermentable sugars from cellulose and hemicellulose with conversion percentages of around 22 and 31%, respectively (Silva-Fernandes et al., 2015). Next, filtration equipment allows the separation of a solid stream, rich in cellulose, and a liquid stream, rich in hemicellulose. While the solid stream will undergo enzymatic hydrolysis treatment, the liquid stream will be treated with a chemical process after hydrolysis. The enzymatic process is characterized using a cocktail of hydrolase enzymes, thus achieving a cellulose to glucose conversion yield of 93.7%, and the conversion of hemicellulose to xylose with a yield of 38.5%. As for the required operating conditions, 50 ºC and continuous agitation during a residence time of 48 h are required (Silva-Fernandes et al., 2015). Regarding the post-hydrolysis chemical process, sulfuric acid will be used, requiring a temperature of 121 ºC to be maintained for a period of 1 hour (Silva-Fernandes et al., 2015). With these operating conditions, yields of around 97% are achieved for the conversion of cellulose into glucose, and 22% for hemicellulose to xylose. After these two pre-treatment stages, a flow rich in sugars is obtained, which will be used in the fermentation stage for the co-production of nisin and lactic acid.

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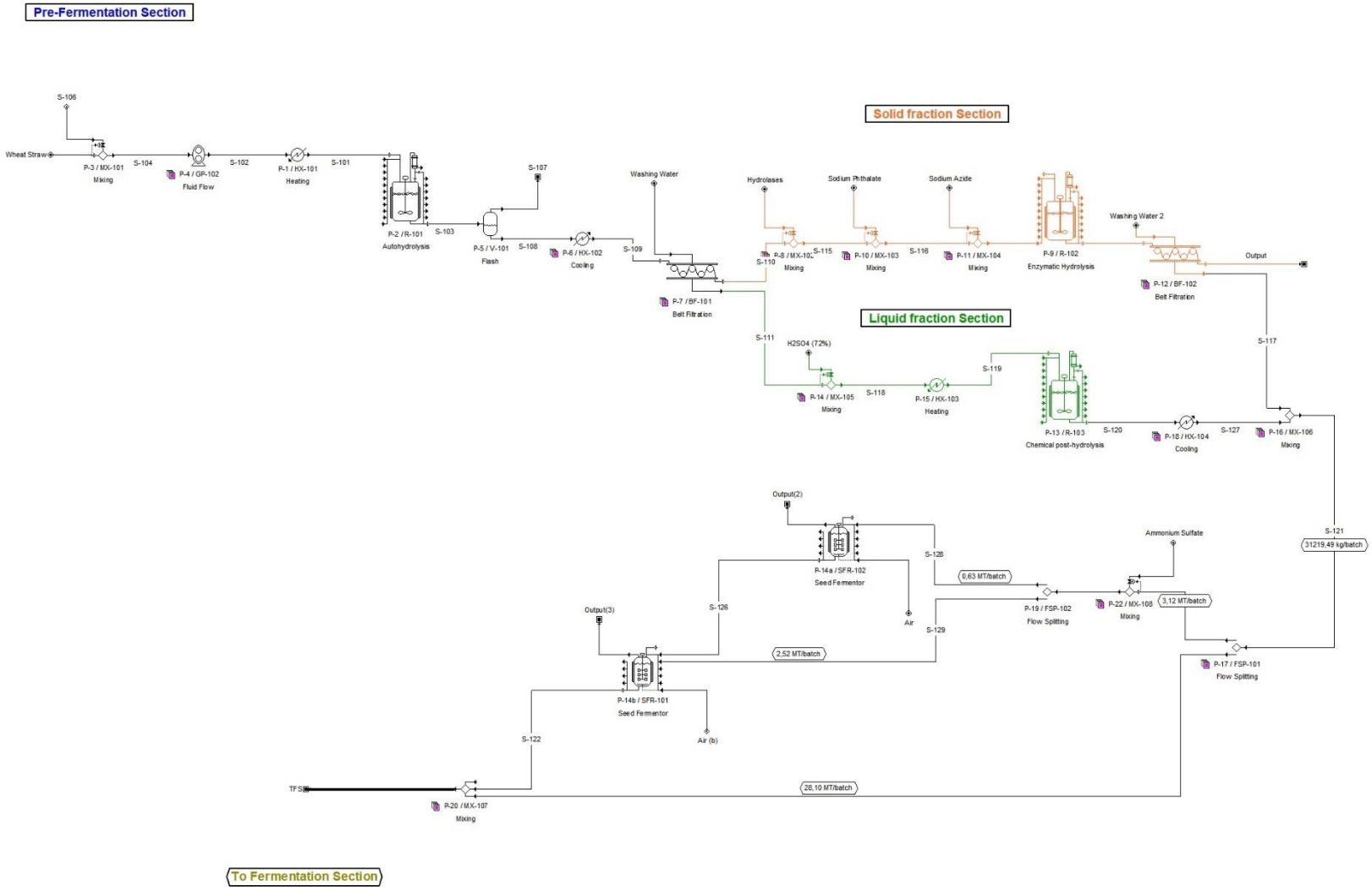

Figure 1. SS1.Pre-treatment flow diagram of PLA-nisin-based functional film process

10.2.2 SS2. Fermentation

The fermentation process is based on the combined production of nisin and lactic acid (as a base element for the production of PLA) by the strain *Lactococcus lactis* (Guerra et al., 2007). One of the most important aspects when considering a fermentation process is the formulation of the culture medium as it not only affects the regulation of the microbial metabolism and thus the productivity and yield of the process, but also the economic viability of the biotechnological process as the production costs are usually strongly related to the formulation of the medium, with percentages between 25-40% of the total (Moo-Young, 2019). While the carbon source will be provided in the form of glucose and xylose, obtained after the wheat straw pre-treatment process, it is necessary to add a source of nitrogen (NH_4OH) and phosphorus (K_2HPO_4). As for the ideal operating conditions to promote a higher yield of the fermentation process, it is necessary to operate at 30 ºC under an aeration flow of 0.5 $L \cdot h^{-1}$ for a period of 24 h (Malvido et al., 2019) (**Figure 2**).

10.2.3 SS3. Downstream

Following the previous fermentation process, two fermentation products, i.e., nisin and lactic acid, are obtained as well as biomass and the residual fraction of the culture medium that has not been depleted. Therefore, a further step for the separation and purification of the two co-products is required (**Figure 2**). First, to separate the biomass, a vacuum filtration system is used, followed by a chemical precipitation in an acid medium, using ammonium sulphate (Tafreshi et al., 2020). This purification system was chosen based on the high nisin recovery achieved. The precipitated nisin will be separated from the stream by a centrifugation system and then the final product will be obtained after spray drying with a purity of more than 95% by weight.

After the centrifugation, a lactic acid rich stream is obtained, which will be processed for separation and purification. Three stages can be distinguished in the purification of lactic acid: a first concentration stage to remove excess water, a second esterification stage with methanol, in which methyl lactate is obtained, which will be reconverted into purified lactic acid in the third stage of hydrolysis (Heliodoro Gil-Horán et al., 2008).

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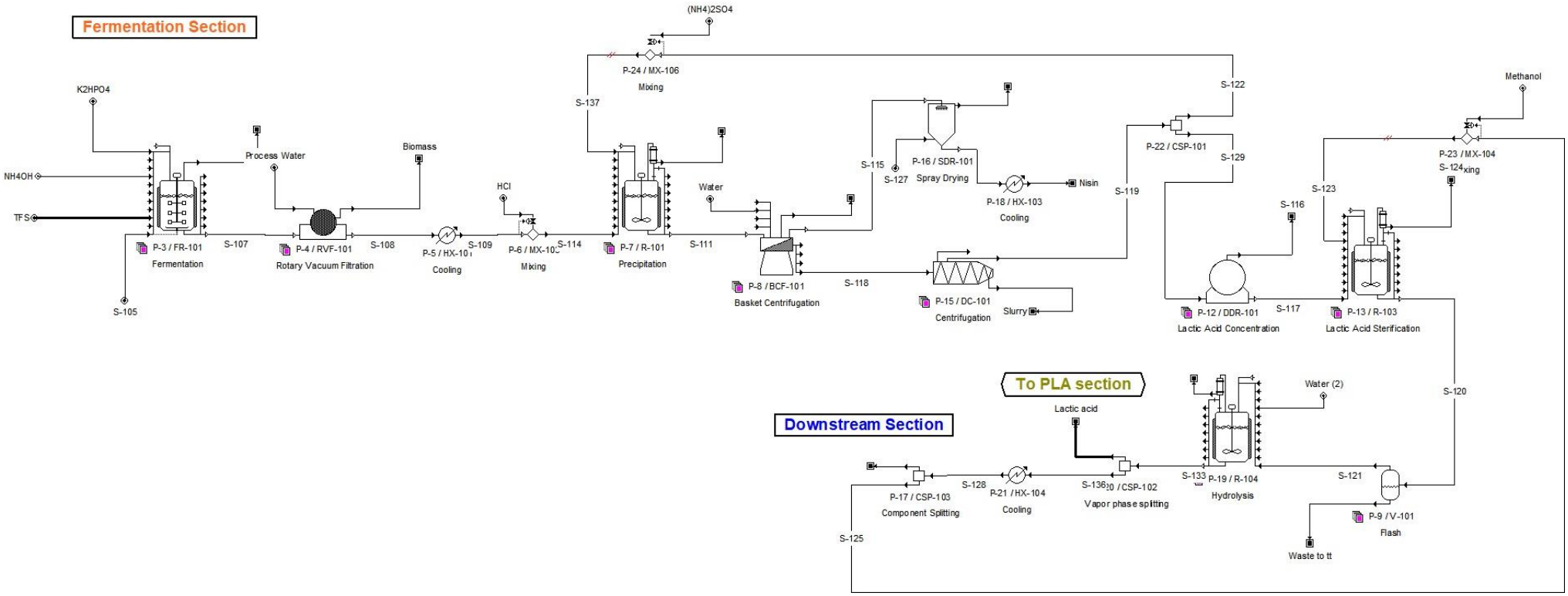

Figure 2. SS2. Fermentation of Wheat Straw and SS3. Downstream Process flow diagram of PLA-nisin-based functional film process

10.2.4 SS4. PLA film production

The production process of high molecular weight PLA from lactic acid is carried out in a sequence of 4 steps (**Figure 3**), which are described below.

10.2.4.1 SS4.1. Oligomerization

The formation of high molecular weight polymers requires the use of highly concentrated monomer solutions, i.e., with low water content (Jin et al., 1997; Li et al., 2020; Stille, 1981). Consequently, the lactic acid monomer will be subjected, in a first stage (SS4.1), to a process under high temperature and vacuum operating conditions, where it will undergo self-esterification, leading to the formation of oligomers (low molecular weight PLA) (Vu et al., 2005). The model reactions that have been considered for the large-scale simulation of this first subsystem (SS4.1) are those developed in **Table 1**, where the yields in the production of lactic acid and oligomers after this first stage are also included.

Table 1. Reaction considered for the large-scale simulation of the process subsystem SS4.1

SS1 Oligomerization		Weight %
Lactic acid	$C_3H_6O_3$	65.43
Oligomer LA1	$2\ C_3H_6O_3 \rightarrow C_6H_{10}O_5 + H_2O$	24.60
Oligomer LA2	$3\ C_3H_6O_3 \rightarrow C_9H_{14}O_7 + 2\ H_2O$	9.96

Oligomerization of lactic acid at 180 °C and 533 mbar for a residence time of 20 min yields a mixture of lactic acid monomer (43 wt.%), the oligomer LA1, corresponding to (SS)-2-[(2-hydroxypropanoyl(oxy)] propanoic acid (24.6 wt.%) and LA2, which is (SSS)-3-hydroxybut-3-en-2-[(2-hydroxypropanoyl(oxy)] propanoate (9.96 wt.%). It must be ensured that the stream has a low water content, as the intermediate cyclic dimer, lactide, required for subsequent PLA production, is an unstable compound in the presence of water, thus affecting the overall yield of the production process.

10.2.4.2 SS4.2. Pre-polymerization

Once the lactic acid oligomers have been obtained, the pre-polymerization stage is carried out. The product obtained by this second subsystem is lactide, a cyclic lactic acid diester with the molecular formula $C_6H_8O_4$, obtained from the dehydration of two lactic acid molecules in the presence of SnO (Tin(II) Oxide) catalyst (Botvin et al., 2020). One of the characteristics of lactide is that there are two stereocenters in its molecular structure, which leads to the formation of three optically active stereoisomers: L-lactide, meso-lactide and D-lactide (Balla et al., 2021). From the model reactions, it is possible to progress on the large-scale simulation of the process (**Table 2**). Lactic acid and its oligomers lead to the formation of three stereoisomers of lactide, together with some side products with different molecular structures.

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Table 2. Reactions considered for large-scale simulation of process subsystem SS4.2

SS2 Pre-polymerization	
Lactic acid > Lactide	$2\ C_3H_6O_3 \rightarrow\ C_6H_8O_4 +\ 2\ H_2O$
LA1 > Lactide	$C_6H_{10}O_5 \rightarrow\ C_6H_8O_4 +\ H_2O$
LA2 > Lactide	$C_9H_{14}O_7 \rightarrow\ C_6H_8O_4 +\ C_3H_6O_3$
Side Products	$(C_3H_6O_3)_n$

All three lactide stereoisomers can be converted to PLA by catalysis. Although semi-crystalline PLA structures would be obtained using any of the three stereoisomers presented, all of which are suitable for application as bioplastics, the yield strength, heat resistance and other mechanical properties of the biofilm obtained depend on the proportions of each stereoisomer. The ratio of lactide stereoisomers in the final PLA film will significantly affect its mechanical and morphological properties. As a lot of L-lactide is present in the PLA film, high crystallinity is achieved, which favors obtaining a less amorphous biofilm, with improved properties, highlighting the strength and stability of the biofilm (Auras et al., 2016). PLA obtained from the L-lactide stereoisomer, called isotactic PLLA, is the most abundant commercially, i.e. the one that is produced industrially in larger quantities, given the excellent mechanical properties of the bioplastic, which is widely spread in its applications (Jiang et al., 2016). Therefore, it is necessary to select those operating conditions that favor a higher production of the L-lactide stereoisomer. Thus, a temperature of 240 ºC and a pressure of 32.5 mbar have been considered, which are maintained for a time of 49 min, resulting in a yield of 91.7% (Botvin et al., 2020), and thus obtaining the following proportion of lactide stereoisomers: 73.7% of L-lactide, 16.5% of meso-lactide and 4.1% of D-lactide.

10.2.4.3 SS4.3. Polymerization

After obtaining lactide, the stereoisomers are converted into high molecular weight PLA from a ring-opening polymerization process in the presence of a precursor and a catalyst. As for the precursor for the lactide ring-opening process, most of them are alcohol-based compounds, such as methanol or 1-dodecanol. However, the high potential of poly(butylene succinate) (PBS) as an initiating agent leads to process yields of up to 84% with 0.001 mol% PBS, as opposed to a yield of 42% using 0.1 mol% 1-dodecanol. On the other hand, as for the most efficient catalyst for this stage of the process, the most used is 0.1 mol% tin (II) 2-ethylhexanoate ($C_{16}H_{30}O_4Sn$). Operating conditions of 0.3 bar, 160 ºC and a reaction time of 4 h have been considered as requirements to achieve a yield of 84% (Pholharn et al., 2019).

10.2.4.4 SS4.4. Purification

The separation of the catalyst required in the pre-polymerisation and polymerisation stages is based on the acid-base reaction between SnO and sodium hydroxide (NaOH), resulting in the formation of sodium stannite ($Na_2[Sn(OH)_6]$), with reduced environmental impacts, thus being less harmful compared to the SnO catalyst (Services and Human, 2005).

On the other hand, with regard to the purification of the polymer produced, it is based on a simple evaporation procedure in which all oligomers that have not been bound to the molecular structure of the PLA polymer are removed, selecting 220 ºC and 0.35 bar as the appropriate operating conditions (Pérez-Cisneros et al., 2015).

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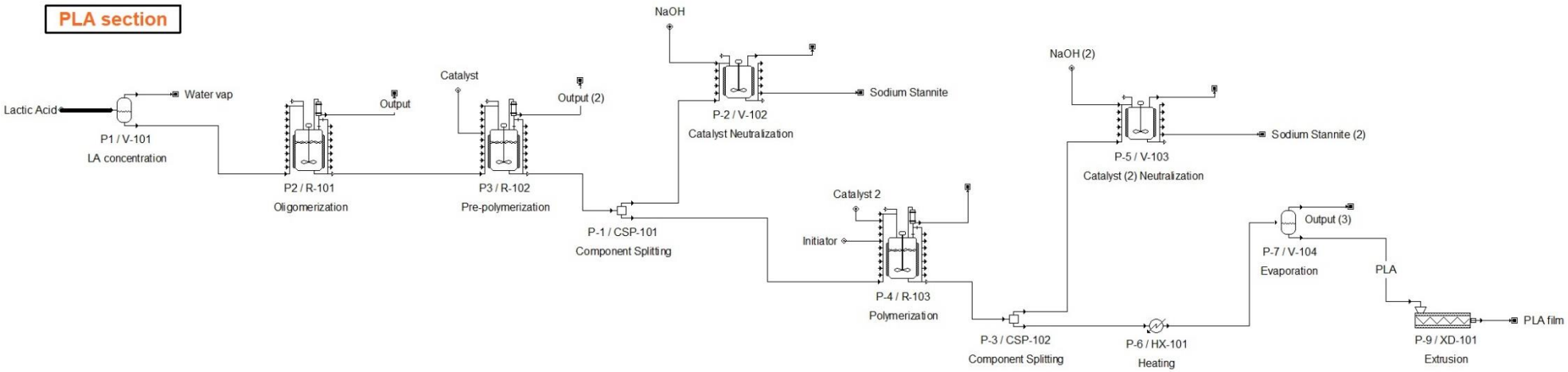

Figure 3. SS4.PLA film production flow diagram of PLA-nisin-based functional film process

10.2.5 SS5. Active packaging film production

The SS5 subsystem has not been simulated on a large scale, nor has it been considered within boundaries of the LCA, since it is considered, a subsequent stage developed by the food packaging company itself, which would be supplied with PLA and nisin films. The process of introducing the bacteriocin into the PLA film layers is based on a simple diffusion coating method, which consists of immersing the PLA films in a solution at pH 2 containing 1% nisin for 18 h, with constant agitation and at room temperature. After this time, the functional films would be washed with a solution of 1 N NaCl and deionized water before drying for subsequent use as food packaging (Jin et al., 2009; Liu et al., 2007).

10.3 Environmental assessment methodologies

In the framework of the evaluation and comparison between the different alternatives of bio-based production processes and their petrochemical analogues, it is important to use a tool that allows the identification of the environmental impacts associated with them (Lindqvist et al., 2019). In this way, it will be possible to analyze the potential and weaknesses of biotechnological processes for replacing those based on the use of fossil resources. In this regard, two methodologies have been used to analyze the environmental performance of the bio-technological production of PLA-nisin biofilms: LCA and Greenness Grid.

LCA has been applied for assessing a modified starch-PLA biofilm (Benetto et al., 2015; Garraín et al., 2007), a chitosan-based film (Leceta et al., 2013), a biodegradable carbohydrate polymer film (Vidal et al., 2007), soy-protein and chitosan-agar films prepared form waste streams and also a wheat gluten-based packaging film (Deng et al., 2013; Leceta et al., 2014). In addition, this methodology has been used to analyze how wastes and food losses could affect the environmental sustainability of food packaging (Pauer et al., 2019).

Although at first glance bio-based processes seem to be more environmentally friendly, this is not always the case. The main "disadvantage" or weak point in the development and implementation of new production processes based on the valorization of agro-industrial waste streams is that they lack the specialization, optimization and development of conventional processes, many of which are based on the use of non-renewable fossil resources for the production of raw materials or energy. Even so, the feasibility of an approach based on circular economy principles needs to be assessed, so that a process is being proposed in which a certain fraction of waste is valorized into a high added value product such as a functional packaging. Moreover, from the perspective of end-of-life management, the biodegradable character of PLA biofilms has to be taken into account, which implies a great ecological and environmental advantage.

On the other hand, looking for define the overall sustainability associated with the active packaging formulated with PLA, as reference bioplastic, and nisin, as antimicrobial, which plays the role of active ingredient that ensures the quality of the stored food, authors have considered the combination of LCA with the Greenness Grid (G2) methodology (Pinto et al., 2020). The basis and fundamentals of these methodologies has been previously defined on **Chapter 3** subsequently, on the following sections the main considerations and data used for its performance are described.

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10.3.1 LCA: Goal and scope

For the evaluation of the environmental profile of the functional biofilm based on PLA and nisin, as there is no data available regarding this production process, a simulation based on experimental data at laboratory scale is required. SuperPro Designer V11.2 has been the selected software, as it allows to perform material and energy balances, which values will be used as inputs for the development of the LCA methodology. The production of 1 kg of PLA-nisin biofilm has been the functional unit selected to report the environmental results. In terms of the scope of the study, an attributional cradle-to-gate approach has been considered, which includes the extraction of raw materials, the biofilm manufacture and management of waste and emissions within the system boundaries.

10.3.2 LCA: Inventory database

Inventory data (LCI) is provided through large-scale simulation of the production process, including raw materials, chemicals, energy needs, both electricity and heat, waste streams and emissions. The Ecoinvent v3.5 database has been chosen as the secondary data source to consider the background activities associated with raw materials, chemicals and waste treatments.

The global inventory data for SS1, SS2 and SS3 are shown in **Table 3**, considering as functional unit the production of 1 kg of PLA. On the other hand, **Table 4** shows the main source of data considered for life cycle inventories.

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Table 3. Life Cycle Inventory for the bio-technological production of PLA nisin functional biofilm

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
SS1. Pre-treatment of wheat straw					
Materials/Fuels			Products		
Wheat Straw	10.60	kg	SS1	44.16	kg
Sulfuric Acid	0.01	kg			
Ammonium Sulfate	2.14	g			
Enzymes	1.31	kg			
Water	30.44	kg	Emissions to air		
Sodium Salts	0.34	kg	Carbon dioxide	0.79	kg
Electricity/Heat					
Heat, steam	71.98	kg	Final Waste Flows		
Electricity	94.94	kWh	Non-hazardous waste	2.95	kg
SS2. Fermentation of wheat straw					
Materials/Fuels			Products		
SS1	44.16	kg	SS2	116.16	kg
Dipotassium Phosphate	7.89	kg			
Ammonium Hydroxide	8.48	kg			
Electricity/Heat			Emissions to air		
Heat, steam	51.03	kg	Carbon dioxide	0.95	kg
Electricity	60.54	kWh	Methanol	0.02	kg
SS3. Downstream Process					
Materials/Fuels			Products		
SS2	116.16	kg	SS3	5.64	kg
Ammonium Sulfate	2.52	kg			
Sulfuric Acid	0.03	kg			
Methanol	0.25	kg			
Hydrochloric Acid	21.96	kg	Final Waste Flows		
Water	21.38	kg	Non-hazardous waste	0.88	kg
Electricity/Heat					
Heat, steam	310.67	kg	Waste to treatment		
Electricity	156.17	kWh	Wastewater	124.87	l
SS4. PLA film production					
Materials/Fuels			Products		
SS3	5.64	kg	PLA	1.00	kg
Sodium Hydroxide	0.23	kg			
Water	3.95	kg	Emissions to air		
Catalyst	22.35	g	Lactic acid	0.14	kg
			L-lactic acid	0.25	kg
Electricity/Heat			Water	4.43	kg
Heat, steam	6.35	kg	Emissions to water		
Electricity	4.65	kWh	Tin Oxide	7.48	g
Cooling energy	1226	kJ	Sodium Stannite	21.72	g

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Table 4. Main EcoInvent data source considering for Life Cycle Inventories

Data required	Data source
Wheat Straw	Straw {RoW}| wheat production | Cut-off, U
Sulfuric Acid	Sulfuric acid {RER}| market for sulfuric acid | Cut-off, U
Ammonium Sulfate	Ammonium sulfate, as N {GLO}| market for | Cut-off, U
Enzymes	Enzyme, Cellulase, Novozyme Celluclast/kg/RER
Water	Tap water {Europe without Switzerland}| market for | Cut-off, U
Sodium Salts	Sodium bicarbonate {GLO}| market for sodium bicarbonate | Cut-off, U
Dipotassium Phosphate	Potassium hydroxide {GLO}| market for | Cut-off, U
Ammonium Hydroxide	Ammonia, liquid {RER}| market for | Cut-off, U
Methanol	Methanol {GLO}| market for | Cut-off, U
Hydrochloric acid	Hydrochloric acid, without water, in 30% solution state {RER}| market for | Cut-off, U
Sodium Hydroxide	Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Cut-off, U
Catalyst	Tin dioxide {GLO}| market for | Cut-off, U
	Electricity/Heat
Electricity	Electricity, medium voltage {Europe without Switzerland}| market group for | Cut-off, U
Heat, steam	Steam, in chemical industry {RER}| market for steam, in chemical industry | Cut-off, U
Cooling energy	Cooling energy {GLO}| market for | Cut-off, U
Wastewater	Wastewater, average {Europe without Switzerland}|market for wastewater, average | Cut-off, U

10.3.3 LCA: Impact assessment and results interpretation

Regarding the methodologies selected for assessing the environmental impacts associated with the manufacture of the biofilm, ReCiPe 2016 hierarchist Midpoint method, to obtain the characterization impact values, and ReCiPe 2016 hierarchist Endpoint method H/H, for comparing the single score values obtained for each process subsystem, have been selected. A total of 18 ReCiPe MidPoint impact categories have been selected for analysis, **Table 5** includes the characterization results and **Figure 4** shows the relative contribution of each process sub-system. In addition, the subsystem with the highest contribution in each of the impact categories is highlighted in bold in **Table 5**.

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Table 5. Characterization results per impact category for each process subsystem

Impact category	Unit	**Total**	**SS1**	**SS2**	**SS3**	**SS4**
GW	kg CO_2 eq	258	66.7	74.7	**112**[1]	4.38
SOD	mg CFC_{11} eq	111	35.2	31.1	**41.9**[1]	2.13
TA	mg SO_2 eq	775	220	225	**316**[1]	13.9
FE	g P eq	102	**41.5**[1]	33.2	25.1	2.68
ME	g N eq	9.01	**3.74**[1]	2.35	2.75	0.17
TET	kg 1.4-DCB	369	53.3	128	**167**[1]	20.7
FET	kg 1.4-DCB	3.35	**1.09**[1]	0.96	0.99	0.31
MET	kg 1.4-DCB	4.74	**1.53**[1]	1.39	1.44	0.39
HCT	kg 1.4-DCB	5.95	**2.22**[1]	1.94	1.62	0.17
HNCT	kg 1.4-DCB	152	**51.0**[1]	44.5	44.1	11.9
FRS	kg oil eq	80.2	18.9	23.2	**36.8**[1]	1.30

The results show that the main contributors to the environmental profile obtained for the process are subsystems SS1 and SS3, with subsystem SS4 being the smallest contributor.

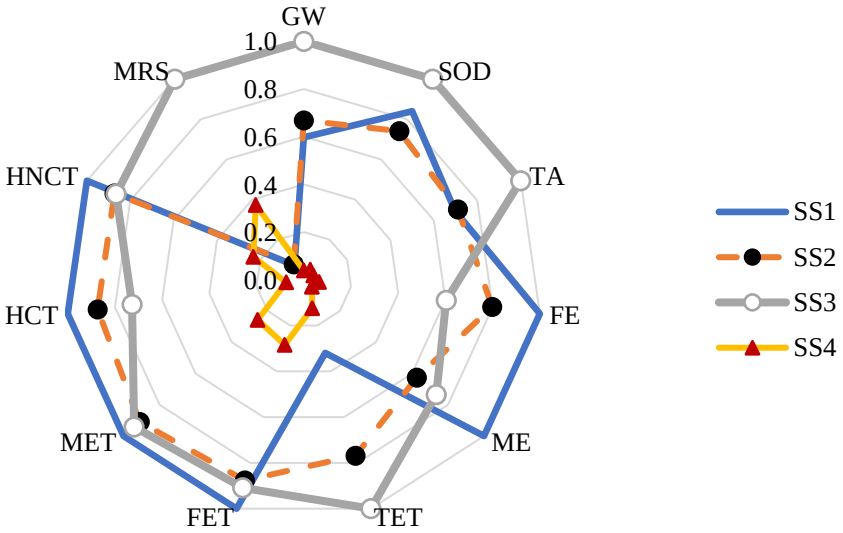

Figure 4. Relative environmental contribution of each process subsystem

Regarding the SS1 and SS2 subsystems, the environmental profiles obtained by applying the ReCipe methodology are shown in **Figure 5** and **Figure 6**, respectively. As can be seen, the main hotspot of the environmental profiles obtained for both SS1 and SS2 is the electricity requirements. As for SS1, the equipment with the highest energy demand is the P-14b seed fermenter (**Figure 5**), which represents 53.6% of the total electricity required for this process subsystem, followed by P-9, the reactor in which the enzymatic hydrolysis of the solid fraction takes place. On the other hand, the contribution of steam in the TET and FRS impact categories is also noteworthy due to its non-renewable nature and the background activities required for its production.

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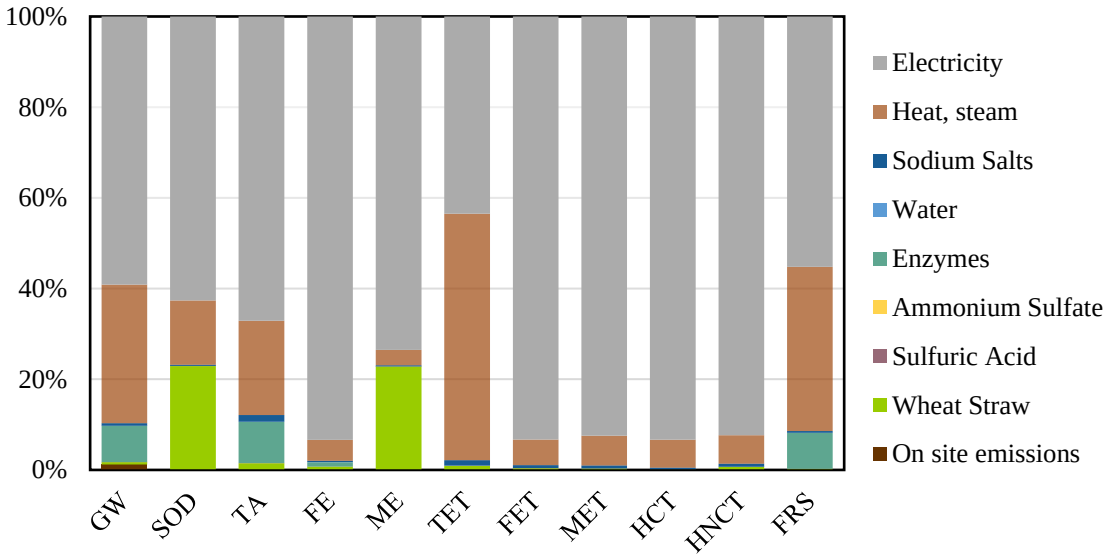

Figure 5. Relative contribution per unit of the process subsystem SS1.

With regard to the SS2 subsystem (**Figure 6**), the one referring to microbial fermentation, the main reason for the high-power demand is based on the need to maintain a homogeneous fermentation medium, through a constant stirring system, during the whole fermentation time, i.e., 24 hours. On the other hand, potassium phosphate also exhibits some impact on the environmental profile obtained, as well as ammonium hydroxide in the TET category. The environmental contributions of these chemical agents are the result of their non-renewable character, which implies the consumption of non-renewable fossil and mineral resources, as well as due to their synthesis processes, which lead not only to the consumption of other chemical agents, but also to energy needs, emissions and waste streams, which entail environmental impacts in the categories studied.

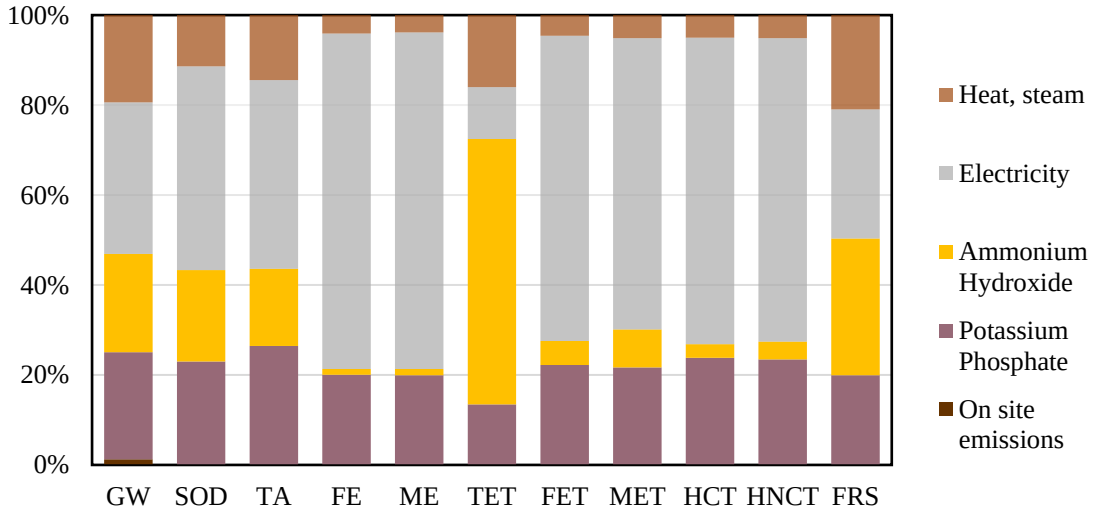

Figure 6. Relative contribution per unit of the process subsystem SS2.

A detailed analysis of the SS3 subsystem has also been carried out (**Figure 7**), where it has been observed that, unlike the previously analyzed subsystems, the calorific requirements are the main hotspot of the profile for most of the impact categories studied,

with the exception of the MRS. In the case of this category, ammonium sulfate is the main contributor, given the significant energy demand required by its production process, obtained by the use of non-renewable resources, causing it depletion.

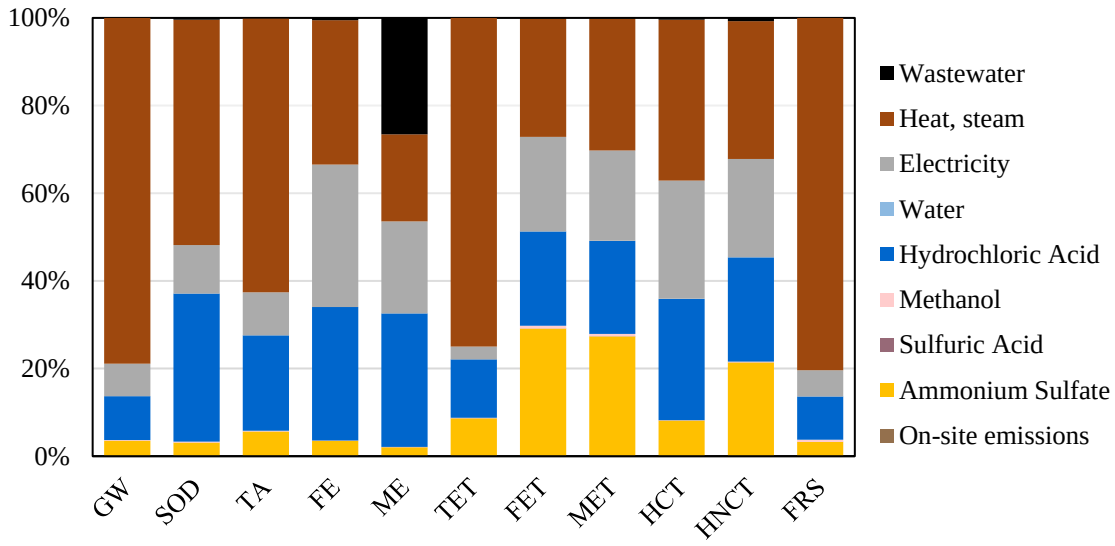

Figure 7. Relative contribution per unit of the process subsystem SS3.

Regarding SS4, the only category in which the SS4 subsystem presents a certain contribution is that of MRS and, in order to find out which component of the subsystem is responsible for this contribution to the overall environmental profile, a detailed analysis of the SS4 subsystem has been carried out, obtaining the profile shown in **Figure 8**. As can be seen, the use of the catalyst is the main hotspot in the MRS impact category, deriving from the background activities associated with its non-renewable origin. On the other hand, its impact on the ecotoxicity categories, both FET and MET, and its impact on human health, especially in the HNC category, is also remarkable. Continuing with the analysis of this subsystem, the electrical requirements give rise to an important contribution in the profile, being the main contributor in the impact categories of GW, SOD, TA, FE, ME and FRS, together with the steam requirements. Its environmental implication is derived from its non-renewable fossil nature, in addition to the production process necessary to obtain them. On the other hand, it highlights the contribution of on-site emissions in the TET impact category, with liquid emissions containing traces of catalyst being the reason for this high environmental contribution.

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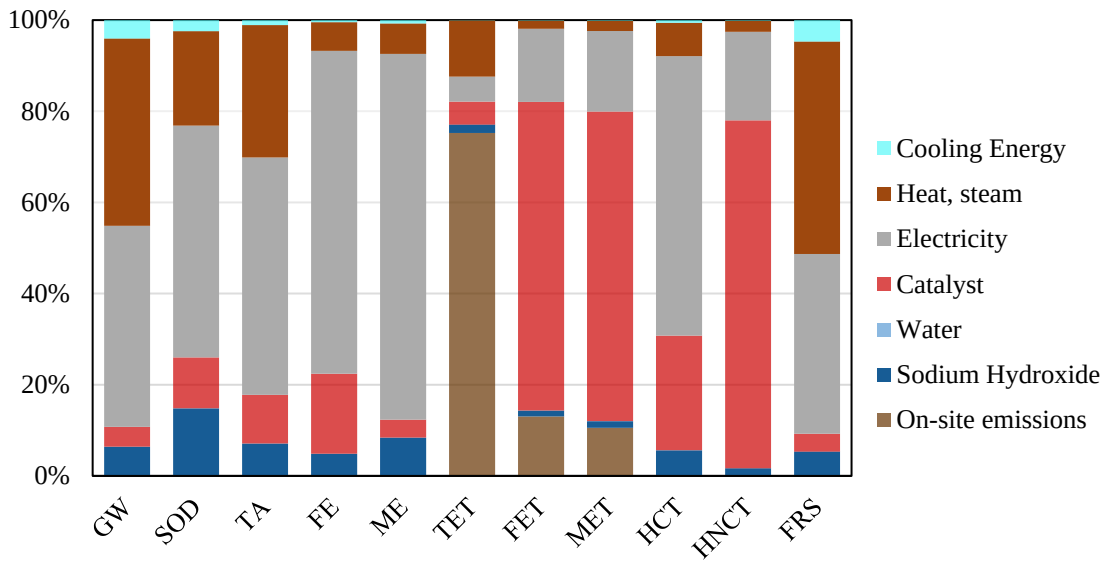

Figure 8. Relative contribution per unit of the process subsystem SS4

Besides the ReCiPe Midpoint methodology, also the EndPoint has been used, in order to compare the environmental contribution of each of the subsystems, grouping the results into three damage categories: human health, ecosystems and resources. The sum of these categories gives rise to obtaining the single score, a dimensionless value indicator in which the overall environmental characterization scores are weighted.

As can be seen in **Table 5**, the SS3 subsystem is the most damaging in all the categories, being that of human health where the greatest impact is observed. In contrast, the SS4 subsystem is the one that, globally, can be considered the most environmentally friendly since its damage values are relatively low.

10.4 Sensitivity assessment

For providing an improved scenario, a sensitivity analysis is developed, based on the hotspots previously identified. The electricity is the main contributor of the environmental profile of the pretreatment section, to this end, the sensitivity assessment is based on (1) reduction on electricity needs by 10%-20%, and (2) promote the use of renewable resources to for electricity production. In this regard, **Figure 9** shows the sensitivity assessment for this first process section.

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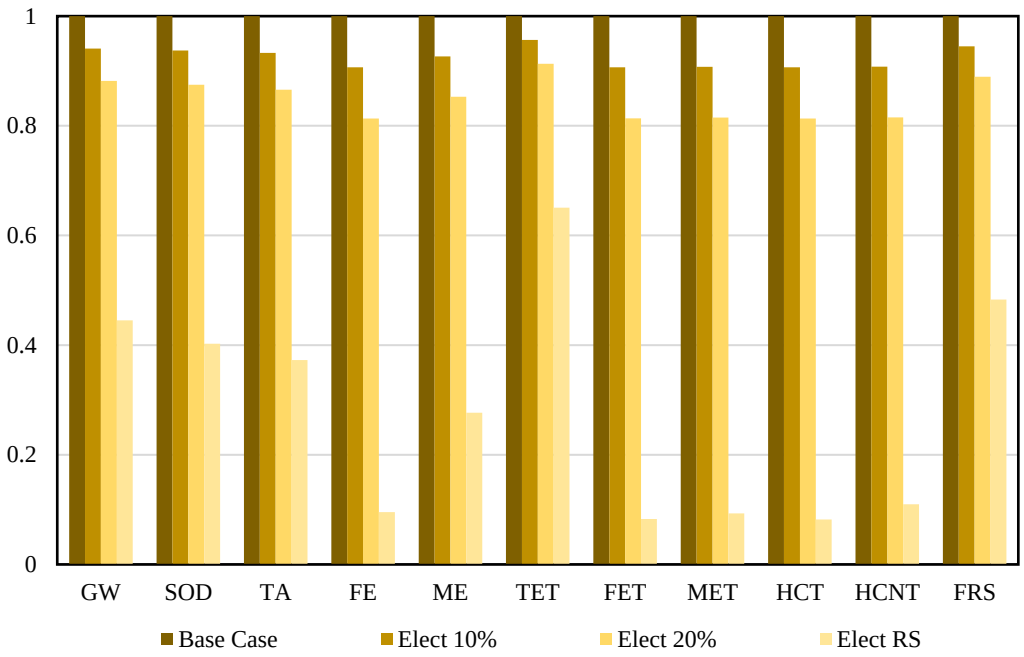

Figure 9. Sensitivity assessment of the environmental profile of the pretreatment section of WS valorization

As expected, the optimization on the use of electricity entails a significant improvement on all the impact categories under evaluation, being the use of electricity coming from renewable resources the most adequate alternative, with impact reduction values between 35% (for TET category) and 90% (for FE impact category). The huge environmental load reductions are observed on the FE, FET, MET HCT and HCN, with reductions between 89% and 92%.

In the case of the SS2 section, the same approach for the electricity has been considered but also, given the huge impact of the use of ammonium hydroxide for the formulation of the fermentation medium, also a sensitivity analysis has been made for assess the impact of its reduction. To this end a reduction on the dose of this compound is evaluated, in the range of 5%-10%, this reduction of the requirements could be achieved by the increase on the productivity and efficiency of the process scheme. With these aspects in mind, **Figure 10** shows the sensitivity assessment for this SS2 process stage.

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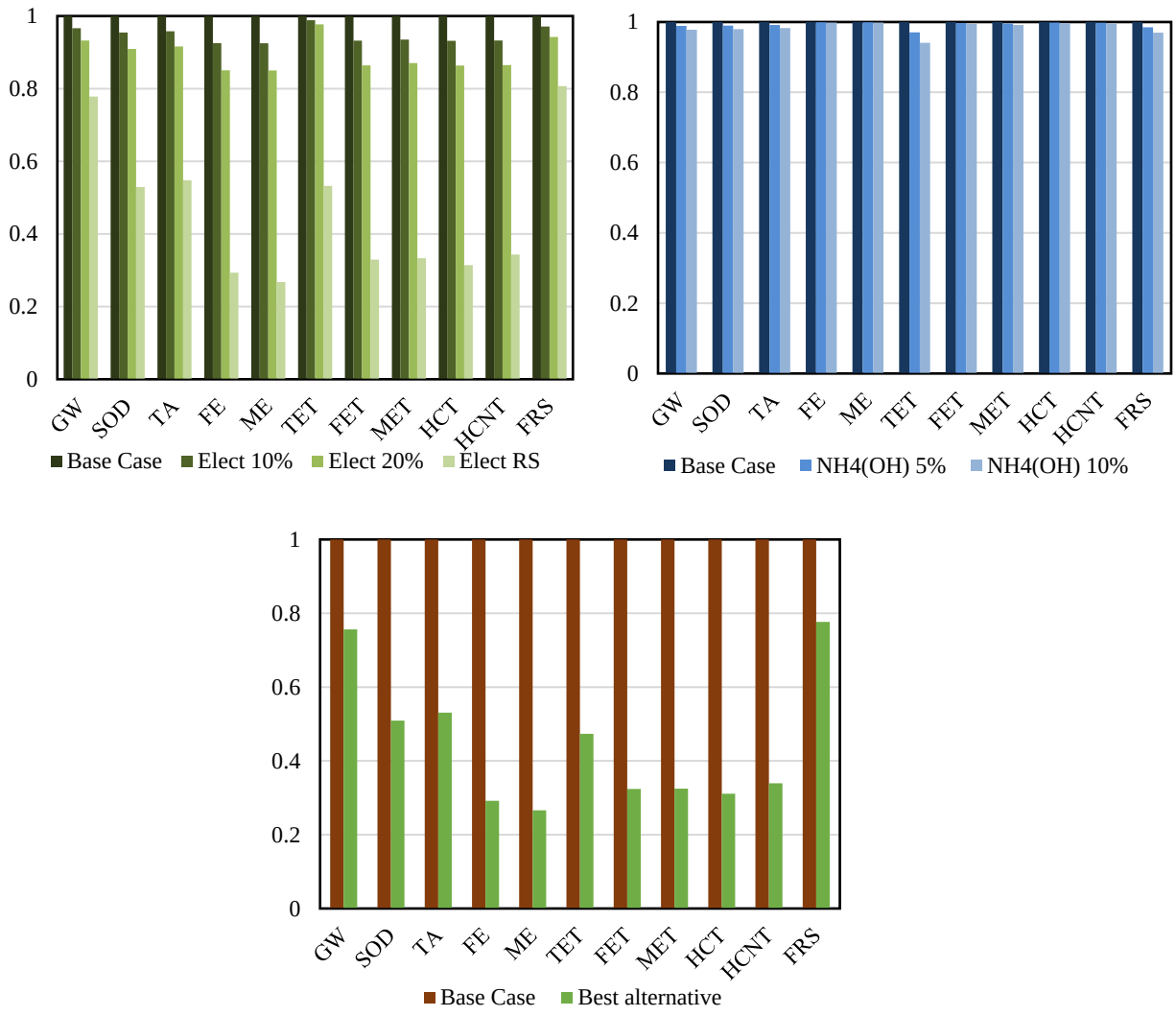

Figure 10. Sensitivity assessment of the WS valorization fermentation section.

The reduction on the needs of electricity implies an outstanding reduction on the environmental loads, in a range between 14% for TET and 73% for ME impact categories, when using renewable resources for electricity production. Besides, the reduction on the dose of ammonium hydroxide does not provide important environmental loads reduction, the highest one achieved is a 3.1% for TA category, but the other impact categories the improvement on the impact are below this value.

On the other hand, by selecting of the best scenario provided by the optimization on the use of electricity (the one considering renewable resources) and by the reduction on the dose of ammonium hydroxide by a 10%, the improvement of the environmental loads is in the range of 21% for FRS impact category and 73% for the ME one. To this end, it could be concluded that a high degree of improvement of the fermentation stage can be achieved.

For the SS3 section, two main approaches could be considered aiming to provide an improved environmental profile: (1) reduction on the use of steam by 10%-20 and (2) use of renewable resources to its production. Also, for the downstream section, an analysis on the use variation of the use of HCl is assessed, considering 5-10% of dose reduction. In this regard, **Figure 11** shows the sensitivity assessment for this first process section.

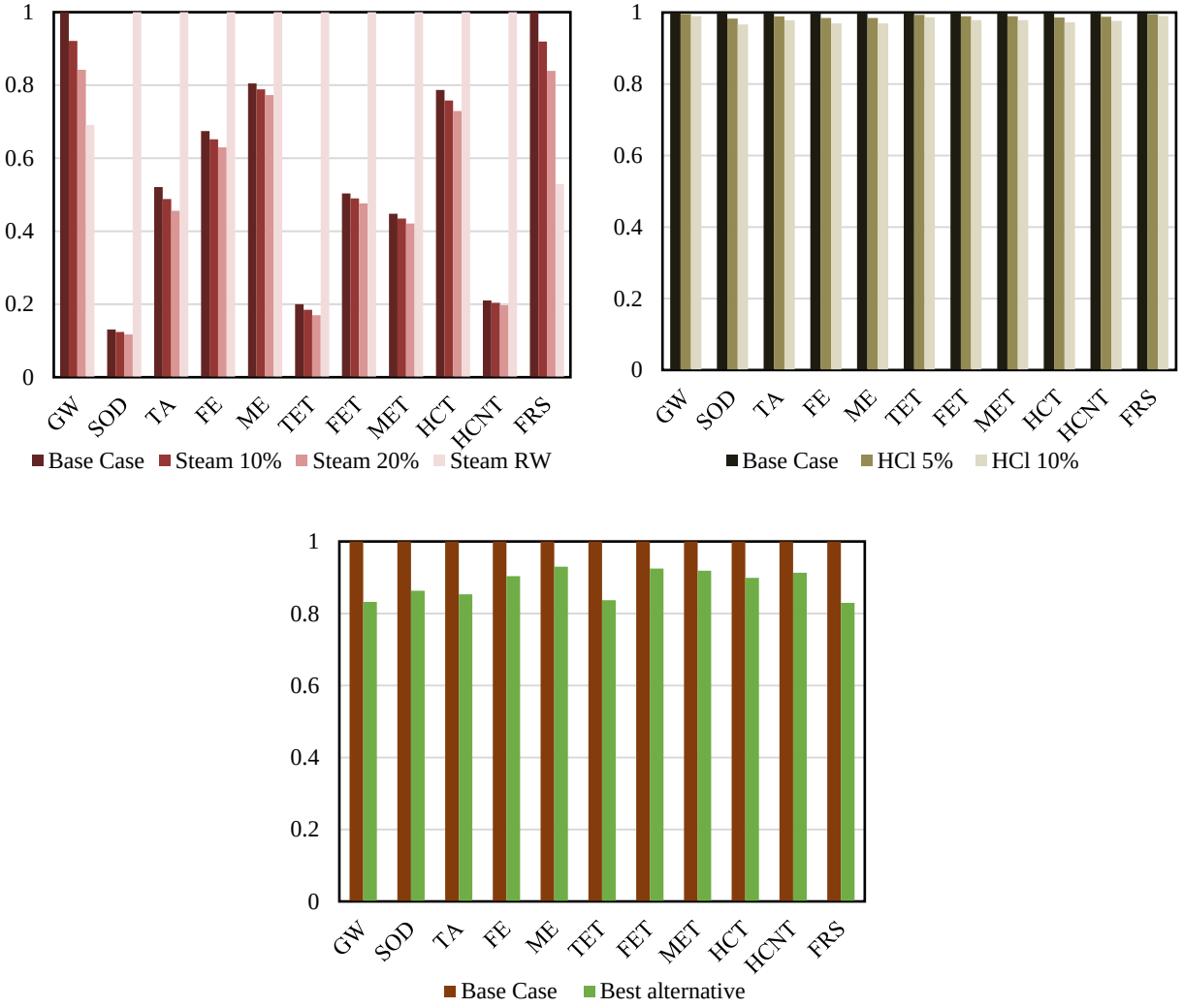

Figure 11. Sensitivity assessment of the WS valorization downstream section.

The reduction on the use of steam requirements by a 20% is the one that promotes a better environmental profile, reaching values above 80% in the HCNT (80%), TET (83%) and SOD (88%) impact categories compared to the base case. On the other hand, the use of steam from renewable energies, in this case from the burning of wood waste in a furnace with a capacity of 50 kW, does not imply an improvement in environmental impact, with the exception of two impact categories: GW, with a 31% reduction compared to the base case, and FRS, reaching values with a 47% environmental improvement. On the other hand, the reduction on the dose of hydrochloric acid does not provide important environmental loads reduction, the highest one achieved is a 3%, but in most of the impact categories the improvement on the impact is below that value.

On the other hand, by the consideration of the best alternative scenarios provided by the optimization on the use of steam (the one considering a 20% reduction on its requirements) and by the reduction on the dose of HCl by a 10%, the improvement of the environmental loads amounts to a 17% for GW and FRS impact categories. Even though the range of environmental improvement is not as high as for the SS2 section, the values

achieved are sufficiently significant to think about the proposed optimized alternative scenarios.

Last of all, for the case of the PLA section, the SS4, **Figure 12** represents the optimization on the use of electricity requirements, as it has been the main hotspot identified for this section in most of the impact categories. It should be mentioned that for the ecotoxicity-related impact categories (TET, FET, MET and HCNT) the main environmental contribution is derived by the use of the catalyst, however a sensitivity analysis around this has not been evaluated since it is necessary to use the catalyst for the manufacture of the PLA biopolymer. The improvement on this load could be achieved by increasing the productivity of the process as, for example, an enhancement of the process yield.

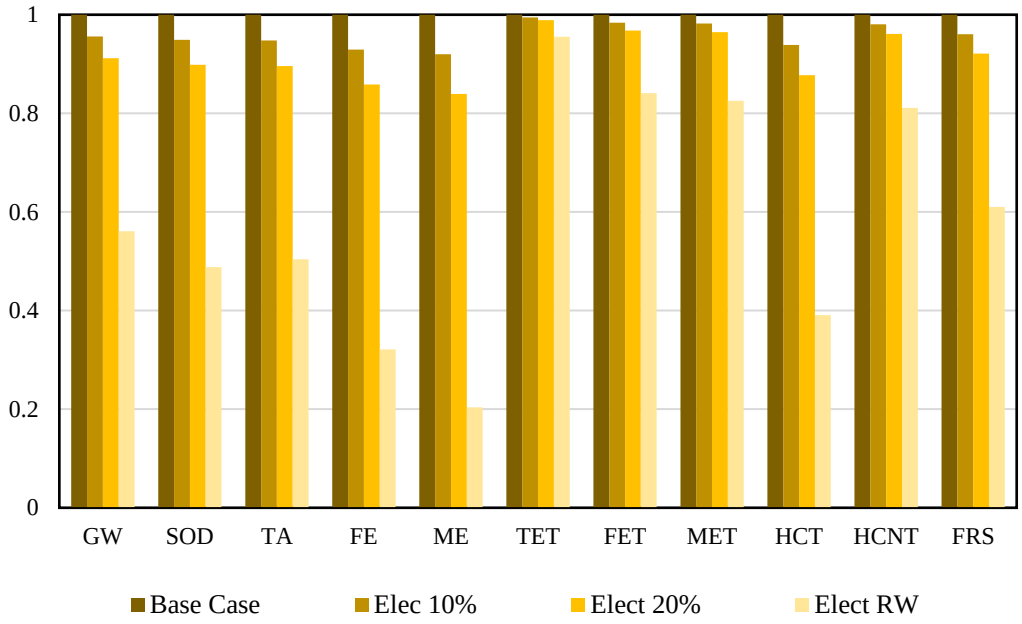

Figure 12. Sensitivity assessment of the WS valorization PLA production section.

Once the sensitivity of all the process stages has been assessed, a global sensitivity is provided, including the best results obtained for each subsystem. In this regard, **Figure 13** represents the base case scenario and its comparison with the optimized one, achieving reduction loads in the range of 27% for the FRS impact category and 64% for the case of FE, with an average of reduction of 46%.

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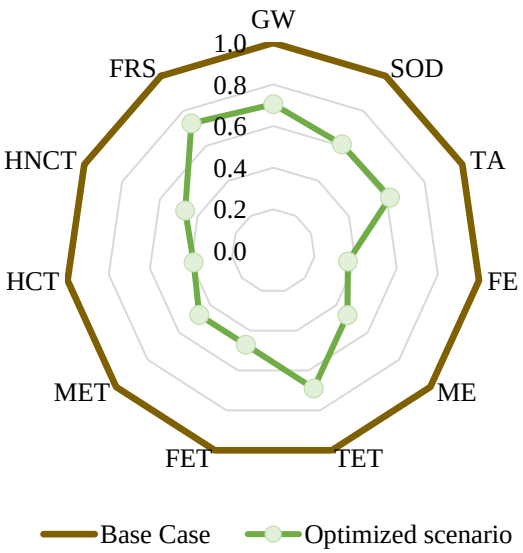

Figure 13. Comparison between the base case scenario and the optimized one, considering the sensitivity assessments.

10.5 G2: Greenness grid results

For the evaluation of the environmental profile of the functional biofilm based on PLA and nisin, as there is no data available regarding this production process, a simulation based on experimental data at laboratory scale is required. SuperPro Designer V11.2 has been the selected software, as it allows to perform material and energy balances, which values will be used as inputs for the development of the LCA methodology.

Obtaining the value of the Green Index requires the development of a series of steps and the calculation of each of the metrics separately. In this way, **Table 6** includes the main data that have been used for the development of the G2 methodology: greenness grid.

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Table 6. Main data required for the development of G2: greenness grid methodology.

Parameter	Value	Parameter	Value
E factor	23.98	Environmental Cost Index	0.60
β_1	32.46	Sustainability Factor	0.93
$f(x, \beta_1)$	0.48	Mass input (kg)	10.60
Energy requirements (kWh/kg product)	38.56	β_7	1.44
Energy price (€/kWh)	0.07	Mass of derivatives (kg)	2.09
$\beta_{6.1}$	0.43	β_8	1.44
Economic Cost Index	$2.95 \cdot 10^{-3}$	Reaction Mass Efficiency	0.55
Environmental Cost (g CO_2/kWh)	430	Productivity	0.29
$\beta_{6.2}$	839	Feedstock	0.26
Body exposure	0.10	Weight (kg)	70

Compound	Hazards	Maximum value			Ratio	SHI[1]
		PH[1]	*HH*[1]	*EH*[1]		
Ammonium Hydroxide	H221, H280, H302, H314, H318, H331, H332, H400	3	4	4	0.01	0.04
Ammonium Sulfate	H402	1	-	-	0.06	0.06
Potassium Phosphate	-	-	-	-	0.01	-
Hydrochloric acid	H302, H314, H318, H335	-	4	-	0.55	2.21
Methanol	H225, H301, H311, H331, H370	3	4	-	0.01	0.03
Sulfuric acid	H314, H318	-	4	-	$7.11 \cdot 10^{-4}$	$2.84 \cdot 10^{-3}$
NaOH	H314, H318, H402	-	4	1	0.01	0.02
SnO	H302, H317, H319, H372	-	2	-	$5.63 \cdot 10^{-4}$	$1.13 \cdot 10^{-3}$

[1]Acronyms: PH: Physical Hazard, HH: Human Hazard, EH: Environmental Hazard, SHI: Substance Hazard Index

Once the data has been processed and each of the metrics has been calculated, they are summed, thus obtaining a value between 0 and 15. **Table 7** shows the values obtained, as well as the final resulting value for the Green Index, reaching a score of 10.93, which is indicative of a potentially sustainable process.

Table 7. Metric score values and global Green Index obtained for PLA-nisin-based film

	Metric	Value	Color Bar		Metric	Value	Color Bar
1	E factor	0.48	Grey	**9**	Catalyst	1.00	Green
2	Atom Economy	1.00	Green	**10**	Degradability	0.00	Red
3	Process Safety	0.50	Grey	**11**	Safety	0.98	Green
4	Reduced Toxicity	1.00	Green	**12**	Accident Prevention	0.75	Blue
5	Safe Solvents	0.98	Green	**13**	Carbon Efficiency	1.00	Green
6	Energy Efficiency	0.30	Orange	**14**	Reaction Efficiency	0.45	Grey
7	Renewable Resources	0.84	Green	**15**	Mass Productivity	1.00	Green
8	Avoided Derivatives	0.65	Blue				
Green Index = 10.93							

This methodology also makes it possible to identify the aspects that need to be addressed in order to obtain a higher value in the index, in other words, a process with a higher degree of sustainability. Two metrics have been identified on which special

attention should be paid, given their low degree of sustainability: energy efficiency and the degradability of the components that form part of the production process. Regarding energy efficiency, the LCA results obtained in the environmental profiles already indicated an environmental problem, given the large impact of the energy consumption required in each of the subsystems. It should be noted that it is possible to develop a large degree of improvement in this aspect with the optimization of processes and energy efficiency, through the selection of less energy-demanding equipment and by carrying out Pinch Analysis, a methodology used to identify the minimum energy consumption necessary for the development of large-scale processes.

10.6 Conclusions

PLA-nisin functional biofilm obtained from the biotechnological valorization of wheat straw has proven to be a sustainable alternative for the replacement of fossil-based plastic films. The large-scale production process has been divided into four subsystems, to which the LCA methodology has been applied, SS3: Downstream stage being the main environmental contributor, with energy requirements identified as the main critical points. In order to reduce the energy requirements of the process, different strategies could be carried out. The first of these, and perhaps the simplest, would be to valorize the biomass obtained after the fermentation process, given that its calorific value is sufficiently high for its valorization in a cogeneration system. In this way, the energy produced could be used in the production process itself, thus reducing the consumption of external fossil energy resources. Besides, a second appropriate strategy would be to carry out a pinch analysis, with the aim of using the process streams, which are at different temperatures, as heat transfer agents, thus reducing the consumption of steam and cooling agents.

In addition, the G2 methodology has been used to analyze the sustainability score of the proposed biotechnological process, obtaining a Green Index value that is indicative of its potential to be considered as a sustainable agricultural waste recovery process. This report provides valuable information for the development of future biotechnological procedures aiming at the valorization of lignocellulosic wastes through the production of active food packaging films. The environmental profiles obtained, together with the main critical points analyzed, could help to identify which actions should be implemented to reduce the impacts associated with the process. Moreover, the use of the Green Index value could be very useful for stakeholders, as it is a unique value, easily understandable by citizens, for the dissemination of new sustainability criteria in food packaging.

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11

Multi-criteria decision map to assess food packaging sustainability

This chapter partially reproduces content already published as "Arias, A., Feijoo, G., Moreira, M. T. (2021). Establishing the multi-criteria roadmap and metrics for the evaluation of active films for food packaging. *Current Research in Green and Sustainable Chemistry*, *4*, 100160.".

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SUMMARY

Food industry is one of the sectors with the highest production volumes, with disposable plastic films being the most widespread packaging method, leading to important environmental problems (i.e. fossil resource depletion and GHG emissions). Within this framework, the development of biodegradable films with antimicrobial properties is of particular interest. This chapter provides a roadmap based on holistic criteria along with quantitative metrics to analyze the opportunities and challenges of bioactive food packaging prototypes. Five main categories have been selected for analysis: packaging evaluation, environmental, circularity, economic and social criteria. The multi-decision criteria map proposed is hoped to be a useful tool for researchers and stakeholders to analyze the suitability of bio-based packaging from the point of view of environmental, technical and consumer health preservation.

Therefore, **Chapter 11** is a methodological guideline that encompasses the main criteria that requires to be assessed when evaluating the suitability of a food packaging. The integration of the different perspectives of sustainability and circularity could enhance the potentiality of new prototypes, and also could help to the identification of the main aspects in which greater efforts should be placed in order to increase the suitability it.

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11.1 Suitable food packaging for the future

The commercialization of food products has gone hand in hand with the massive use of plastic packaging/films characterized as single-use or disposable, which generates a huge volume of plastic waste. In absolute terms, out of a total of 500 billion plastic bags and packaging, only 3% recycled (Sabharwal et al., 2018). This leads to an environmental problem, not only because of the fossil resources needed to produce plastic-based films, but also because the final management mostly relies on landfill and incineration, leading to air pollution and impacts on human health (Wu et al., 2018). At present, the development of biodegradable film packaging has become a necessity. Mainly produced via extrusion process (Hajinezhad et al., 2020; Huang et al., 2019; Lyu et al., 2019), the end product is a structured film that allows the controlled dosing of antimicrobial agents included in the polymeric matrix. The most widespread biodegradable packaging is polylactic acid (PLA) (Motelica et al., 2020; Munteanu et al., 2018; Mustăţea et al., 2019; Settier-Ramírez et al., 2021), starch (Akhter et al., 2019; Cottet et al., 2021; de Oliveira et al., 2020; Lubis et al., 2021; Mlalila et al., 2018) and cellulose fibers (Dairi et al., 2019; Ludwicka et al., 2020; Wu et al., 2018).

Other aspects to be considered in food management, handling and packaging is food safety. It is estimated that approximately 30% of people living in industrialized countries suffer food poisoning each year associated with the consumption of spoiled products. In the search for healthier processing alternatives with lower chemical additive content, a variety of options have been considered; from physical processes such as freezing, thermal processing, refrigeration and vacuum packaging, to the dosing of natural-based antimicrobial agents that preserve the quality of the final product (Woraprayote et al., 2018).

The latter, besides being better accepted by consumers, are not subject to regulations as restrictive as those of synthetic-chemical base (Degli Esposti et al., 2018) and increase the functionality of packaging systems by adding new properties (antioxidant, antimicrobial and organoleptic) (Dairi et al., 2019). In fact, the use of antimicrobial packaging films has been reported to be a suitable method for active control of fungal and bacterial growth (Motelica et al., 2020). The inclusion of microbial preservative agents in food packaging can be developed around the following methodologies: incorporating them directly on the polymeric matrix (Kamaruzzaman et al., 2019), developing oxidation reactions from surface irradiation (Adlhart et al., 2018; Correa et al., 2019) or introducing them in the form of polymeric resins with encapsulated nanoparticles (Amin et al., 2020; Chandrakasan et al., 2019; Fahmy et al., 2020; Razavi et al., 2020; Zhu et al., 2021). When developing renewable antimicrobial food packaging films, commonly referred to as "active packaging" (Bourakadi et al., 2019; Monjazeb Marvdashti et al., 2019; Soltani Firouz et al., 2021) or "functional packaging" (Akhter et al., 2019; Kouhi et al., 2020), it should be considered that such films should ensure the following properties: biodegradability, good mechanical and barrier characteristics, antibacterial, availability, economic and technical feasibility, among others (Ali et al., 2019; Bhargava et al., 2020; Espitia et al., 2019; Guimarães et al., 2020; Ludwicka et al., 2020; Mlalila et al., 2018; Rydz et al., 2020)

11.2 Metrics selected for the multi-criteria roadmap.

The direct discarding of waste entails the loss of the possibility of obtaining economic value from its valorization. The implementation of valorization strategies through the development of biorefinery production processes and through the implementation of circular economy actions not only avoids the loss of value, but also contributes to avoid

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the environmental burdens caused by inadequate waste management (Capanoglu et al., 2022). In fact, the implementation of circular economy strategies contributes to sustainability, as the entire forestry and agri-food supply chain will be able to retro-feeding and reduce the consumption of resources.

The procedure followed to carry out this review is developed in three main steps: a first literature review, using Scopus as the main database, in which the articles have been classified according to the type of article (Reviews vs. Experimental Studies). In this screening phase, a final portfolio of 98 papers was compiled. A second step considers the classification of the previously selected experimental studies according to the following categories: film packaging material, antimicrobial/antioxidant agent used, strains selected for film evaluation and field of application. Therefore, in the last step, the selection of criteria was presented, classified into five major categories: Packaging Evaluation Criteria, Environmental Criteria, Circularity Criteria, Economic Criteria and Social Criteria.

In a first attempt to establish an appropriate criterion to develop a suitable prototype for bio-based food packaging, an analysis of available experimental studies has been developed, aiming to define the main trends, bottlenecks and perspectives in this area of knowledge.

For this purpose, the VosViewer software has been used, which allows, through an analysis of the keywords selected by the authors, the identification of the main parameters considered crucial in the development of bio-based food packaging prototypes. While it should be noted that these research articles focus on the laboratory level, where the performance, quality and effectiveness of the films are prioritized, other parameters emerge as being of particular interest: technical and economic feasibility of the large-scale production process, environmental concerns and social acceptance.

The first analysis of the bibliographic data resulted in 323 keywords (**Figure 14**, a), related to each other by the concurrence. Handling such a large number of keywords is impractical and unhelpful. It is therefore necessary to review the keywords in greater detail to identify those that are significant and representative of the different approaches. Therefore, a standardization of the keywords was carried out, classifying them in analogous terms, thus reducing the map file (**Figure 14**, b), until a final concurrence value of 28 was obtained (**Figure 14**, c).

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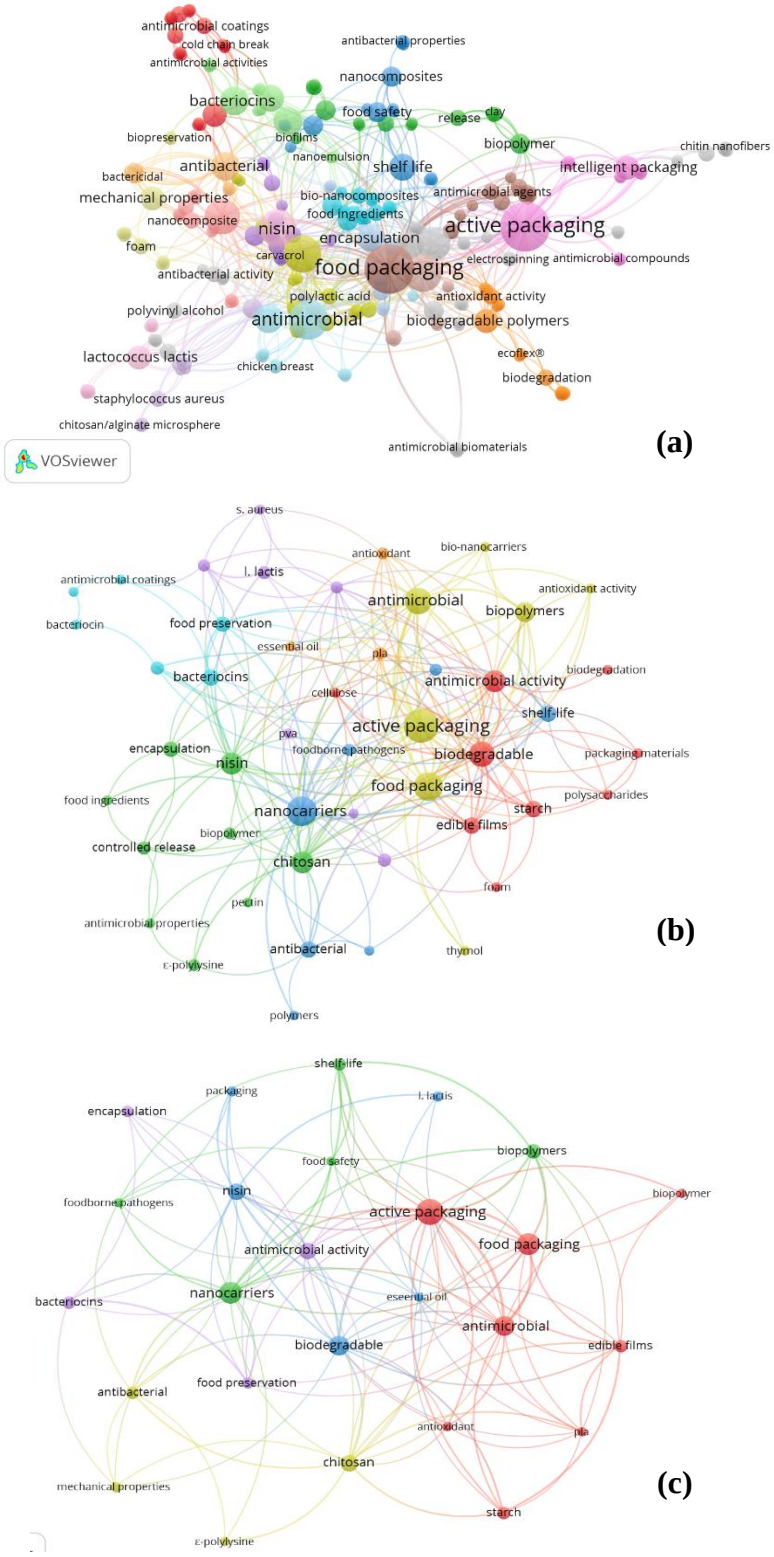

Figure 14. Comparison between the base case scenario and the optimized one, considering the sensitivity assessments. Source: Own elaboration.

Regarding the renewable raw materials selected for the production of the films, the use of PLA, chitosan and starch is recurrent. On the other hand, the use of antimicrobial agents as a method of food preservation is also a key point in the development of new bio-based packaging prototypes, with nisin and essential oils standing out. In addition, with respect to the mode of addition of preservatives, the use of nanocarriers and encapsulation techniques seem to be the most developed by researchers. In this regard, five main criteria have been selected for the evaluation of the suitability of a bio-based packaging prototype.

11.2.1 Criteria selected to evaluate the preliminary packaging prototype

New bio-based packaging prototypes must meet a series of characteristics to be suitable and effective, both from the point of view of providing safe food for consumption and in their design parameters, which not only have to comply with market requirements, but also in this preliminary phase the circularity criteria must be considered, i.e., designing the product to facilitate its subsequent reuse, its degradability and its management as waste.

A preliminary food packaging design should be in accordance with the EU Framework regulation, that broadly defines how are the minimum requirements of the package's materials in contact with the food products. The two regulations that stands out are the: (EC) No. 1935/2004 and (EC) No. 2023/2006 on GMP (Good Manufacturing Practice guidelines). In the case of the first one, its aim is to ensure the effectiveness of the food packaging for the function they were created for, bearing in mind the need of providing, at least, the minimum securing level of protection for human health and consumers' interests. In this regulation the definition of active food packaging is embedded, described as materials that intends to increase the shelf-life and maintain the quality of the products stored inside. In this context, it also includes as series of specific requirements for the case of active packaging, being the need to conserve the composition characteristics and organoleptic properties of the food and the appropriate and the requisite of indicate specifically the parts of the packaging that are categorized as active.

For the case of (EC) No. 2023/2006, the GMP is defined as "those aspects of quality assurance which ensure that materials are consistently produced and controlled to ensure conformity with the rules and with the quality standards appropriate to their intended use". A term included in the regulation, which is particularly in line with the amount of waste generated by the packaging end-of-life, is about plastic recycling, for which the assurance of quality is needed to be demonstrated, documented and monitored in line with the quality policy manual, quality control plans, test and analytical protocols, and the evidence that, indeed, all the legal exigencies are being met.

Based on the previous regards, a total of 6 requisites have been selected for this preliminary assessment. If the outcomes lead to promising results, the evaluation of the subsequent criteria could be performed. If this is not the case, a redesign and improvement of the proposed prototype will be required.

11.2.2 Criteria selected for environmental assessment.

Within the manufacture of plastic-based packaging, the main impacts are focused on the consumption of non-renewable resources and the emissions resulting from their extraction and the production process. The release of polluting compounds affects not only the "health" of the atmospheric environment, but also the quality of the soil of crop areas, affecting in turn the safety and quality of food products. On the other hand, inadequate management of waste streams, as well as uncontrolled waste disposal, can

lead to significant health hazards, as well as pollution of surface and groundwater, and significant landscape impacts.

Besides, given its low decomposition capacity, its presence in the environment causes the release of toxic substances into the soil, its incineration causes environmental pollution and also affects human health due to the emission of carcinogenic toxic substances, among others.

Therefore, the environmental assessment of the different alternatives of bio-based packaging prototypes must evaluate the environmental criteria throughout their life cycle. Thus, in this evaluation stage, it is proposed to perform a LCA to evaluate the following impact categories: Climate Change, Fossil Resource Scarcity, Stratospheric Ozone Depletion, Ecotoxicity and Human Health, among others, as are the ones more assessed on the bibliographic references. On the other hand, two main system boundaries are considered when evaluating the environmental profile of bio-based packaging, cradle-to-gate and cradle-to-grave, while for the methodologies for calculation the uses are diverse (**Table 8**).

Table 8. Recent reports on environmental assessment of bio-based packaging

Reference	System boundaries	Methodology	Product	Use/feedstock
(Cappiello et al., 2022)	Cradle-to-grave	ILCD 2011	PLA + PBS	Milk packaging to 30 days shelf life
(Tamburini et al., 2021)	Cradle-to-grave	ReCiPe MidPoint (H)	PLA	Water bottle 500-750 mL, timeframe of 1 year
(Benavides et al., 2020)	Cradle-to-gate and cradle-to-grave	GREET model	PLA and bio-PE	Food packaging, landfilling/composting for end-of-life
(Bello et al., 2020)	Cradle-to-gate	ReCiPe MidPoint (H)	FDCA as precursor for bio-PEF	Wood and lignocellulosic residues as feedstocks
(Operato et al., 2023)	Cradle-to-gate	CML-IA and Cumulative Energy Demand	PLA	Green composites using pine needles and kenaf fibers
(Fico et al., 2022)	Cradle-to-gate	CML-IA baseline	PLA	Composites of PLA with olive wood waste
(Riofrio et al., 2022)	Cradle-to-grave and cradle-to-gate	ILCD 2011	PLA	Sugar cane as feedstock
(Bishop et al., 2021)	Cradle-to-grave	IPCC, accumulated exceedance, EUTREND and Impact 2002+	PLA	Fresh food packaging using waste resources as feedstock
(Moretti et al., 2021)	Cradle-to-grave	IPCC 2013, GWP 100a	PLA	PLA single-use cups
(Kachrimanidou et al., 2021)	Cradle-to-gate	CML 2001	PHB	Sunflower-based biodiesel industry by-products
(Kookos et al., 2019)	Cradle-to-gate	CML 2001	PHB	Bio-PHB from soybean oil and sucrose as C-sources
(Fernández-Dacosta et al., 2015)	Cradle-to-gate	IPCC	PHB	Wastewater from paper mill and food industry as feedstock

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11.2.3 Criteria for circularity assessment

"Maintain the value of products, materials and resources for as long as possible by returning them into the product cycle at the end of their use, while minimizing the generation of waste" is the way in which European Commission defines circular economy. Following this statement, the criteria for assessing circularity should encompass, at least, the concepts included in the definition of circular economy itself, so that the performed analysis is complete and adequate. As a result, based on this premise, it has been considered that the recyclability capacity, the recovery of non-usable resources, the reuse rate, the use of waste streams, in addition to promoting the use of renewable resources, are the key points on which the criteria to be assessed must be established. It is important to mention that researchers and developers should consider, in the early design phases, the development of products that give up the linear trend of production and single-use products, and that promote efficient designs, easily reusable and, if possible, with multipurpose applications.

Recent research reports have assessed the circularity on the production of bio-plastics (Bellini et al., 2022; Melchor-Martínez et al., 2022; Merchan et al., 2022; Merino et al., 2022; Rosenboom et al., 2022; Visco et al., 2022; Zoghbi et al., 2023). Its main discussions and assessments have been used as a first approach for the definition of the multi-criteria roadmap.

11.2.4 Criteria for economic assessment

New product prototypes should be developed considering an Inclusive Green Economy (IGE). This concept encompasses the terms of human well-being, social equity, environmental risk reduction and ecological scarcity. Green economies are the appropriate vehicle to achieve the goals of the 2030 Agenda and sustainability, seeking a new concept of economic development through the use of smart policies that simultaneously improve environmental quality and human development, focusing on new processes with low ecological footprints.

In order to determine whether the bio-based packaging prototype is viable in economic terms, it is necessary to perform an evaluation of financial metrics, considering the Net Present Value (NPV), Internal Rate of Return (IRR) and minimum selling prices parameters, among others (**Table 9**). If the proposed prototype achieves adequate values of these parameters, then a Life Cycle Cost (LCC) assessment could be developed by extending the scope of the assessment to all life cycle stages.

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Table 9. Recent reports on economic assessment of bio-based packaging

Reference	Feedstock	Product	Economic assessment[1]	MSP[1]
(Rajendran and Han, 2023)	Food waste	PBS	Techno-economic analysis (MSP, ROI, IRR)	3.50 $/kg
(Tassinari et al., 2023)	Agro-food waste	PLA-PHB	Cost-benefit analysis	9.7-37.2 €/kg
(Price et al., 2022)	Cyanobacteria	PHB	Techno-economic analysis	18.34 $/kg
(Izaguirre et al., 2021)	Municipal solid waste	PHB	Techno-economic (total capital cost, annual production cost and revenues estimation)	4.00 $/kg
(Roux and Varrone, 2021)	Waste feed streams	PEF, PTT	Discounted cumulative cash flow analysis	3.13 $/kg
(Kwan et al., 2018)	Food waste	PLA	Techno-economic (ANP, payback, IRR, NPV, MSP)	3.30 $/kg
(Ratshoshi et al., 2021)	Sugarcane waste	PLA, PBS	Techno-economic (MSP, IRR)	2.98 $/kg
(Ioannidou et al., 2022)	Agro-food residues	PLA, PBS	Techno-economic risk analysis	1.42-1.72 $/kg

[1]TEA (techno-economic assessment), MSP (minimum selling price), ROI (return on investment), IRR (internal rate of return), ANP (annual net profit), NPV (net present value).

11.2.5 Criteria selected for social evaluation

Consumers' environmental concerns are increasing, and the concept of green purchasing and sustainable consumption are incorporated into product selection criteria (**Table 10**). Green consumption is based on the purchase of products with a reduced negative impact on the environment. Moreover, authorities should pay attention to how to disseminate information in an appropriate, understandable and accessible way to consumers, based on clear and concise labeling, informing about the key aspects that have been taken into account in the development of the product, from the point of view of sustainability, circularity and environmental and health protection.

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Table 10. Recent reports on social assessment of bio-based packaging

Reference	Social issue	Plastic	Topic assessed
(Niyommaneerat et al., 2023)	Corporate social responsibility	Plastic waste recycling	Sustainability and circularity indicators
(Dorigoni and Bonini, 2023)	Social-norm to increase pro-environmental behavior	Water bottles or tap water?	The contribution of policy-makers interventions to increase the consumption of tap water
(Sundqvist-Andberg and Åkerman, 2021)	Social concerns on food plastic packaging life cycle	Food packaging	Environmental policy design for plastic-based food packaging
(Boz et al., 2020)	Consumer position on sustainable packaging	Packaging value chain	Consumer preferences, sustainable behaviors, perceptions of bio-based packaging materials.
(Notaro et al., 2022)	Consumers acceptance of bioplastics	Bio-based plastic from wood residues	Consumer's attitudes with bioplastic products: quality, environmental and economic approaches
(Orset et al., 2017)	Response to environmental policies	Plastic water bottles	Consumers' willingness to pay and purchasing decisions
(Situmorang et al., 2020)	College students concern	Plastic waste problems	Students' behavior on reducing plastic waste: social and environmental issues

11.3 Multi-criteria decision map according to the selected criteria

Figure 15 is intended to represent the decision tree that includes environmental, circularity, economic and social indicators for the evaluation of the profile associated with bio-based plastics. It is necessary to take into account that within each category several requirements of recommended compliance have been considered. If the target product fails to fulfill requirements, it would be necessary to rethink the prototype and propose modifications to improve the profile.

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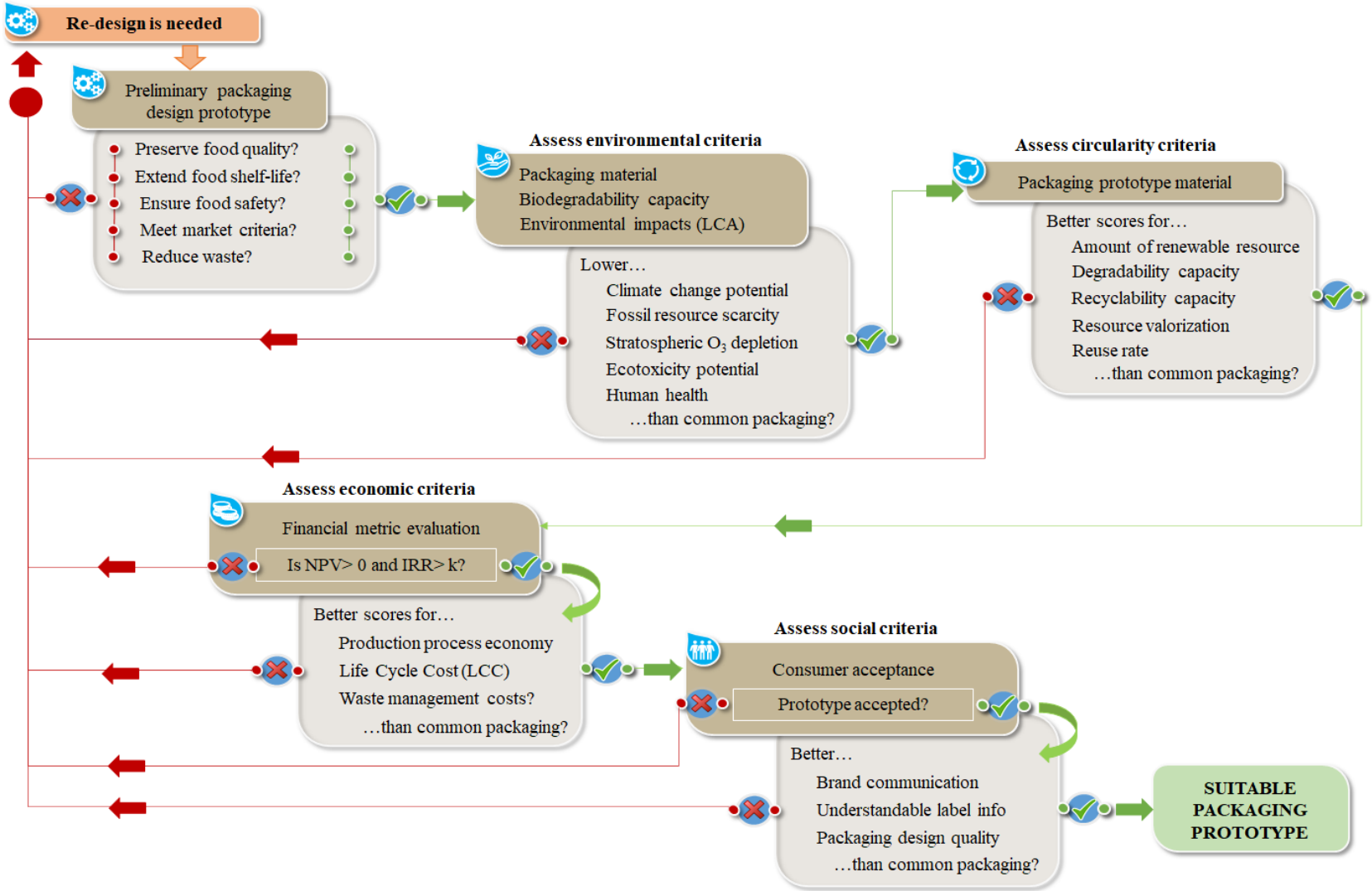

Figure 15. Multi-criteria roadmap to assess the suitability of a packaging prototype. Source: Own elaboration.

11.4 The multi-criteria decision map under assessment

The multi-criteria roadmap has been applied to two alternative active food packaging bio-film scenarios in order to evaluate the sustainability indicators and metrics identified: (1) bio-packaging produced by using corn starch, PVA and glycerol in the packaging formulation and nisin Z, maleic anhydride and cellulose nanocrystals as bioactive agents (de Oliveira et al., 2020). This report highlights the use of renewable resources and waste (corn starch and cellulose pulp, respectively), the biodegradability of the packaging as well as its potential to prevent the proliferation of pathogens and extend the shelf life of food products. The mechanical properties (water vapor and oxygen permeability, swelling index, film homogeneity, among others) are adequate and may represent an excellent alternative to replace traditional plastic packaging. (2) The bio-active film developed in **Chapter 10**, based on a PLA film produced by wheat straw residues and activated by introducing nisin.

With this information, the analysis of this proposal has been developed using the multi-decision criteria map (**Figure 15**). The evaluation is displayed in **Table 11**, for scenario (1) and **Table 12** for scenario (2).

Table 11. Applying the multicriteria roadmap to a bibliographic bio-packaging scenario

Assessment of Packaging Evaluation Criteria	
Food preservation	Yes
Extend food shelf-life	Yes
Ensure food safety	Yes
Reduce wastes and losses	Yes, due to its biodegradability potential and due to the use of waste resources for its fabrication
Meets market criteria	Yes
Preservation agents	Active packaging: Nisin Z, cellulose nanocrystals, maleic anhydride.
Assessment of Environmental Criteria	
Packaging material	Renewable and waste valorization resources
Biodegradability capacity	Yes
Environmental impacts	Reduced, due to the use of renewable resources and due to the valorization of waste streams
Assessment of Circularity Criteria	
Degradability capacity	Yes
Recyclability capacity	Yes
Resource valorization	Yes: cellulose pulp from *Pinnus spp.*
Use of waste streams	Yes: cellulose pulp from *Pinnus spp.*
Reuse rate	Not evaluated
Assessment of Economic Criteria	
Financial metrics evaluation	Recovery of waste from renewable resources reduces the cost of raw materials compared to traditional plastic packaging.
Production process economy	Beyond the NPV and IRR values, the economic viability of the process must be assured.
Life Cycle Cost	Should be adequate due to the previous statements
Waste management costs	Reduced, due to the biodegradability and low toxicity of the packaging materials
Assessment of Social Criteria	
Consumer acceptance	Yes, as a biodegradable, environmentally friendly and functional food-packaging film is developed
Packaging design quality	Mechanical properties evaluation showed good packaging quality
Brand communication	Not evaluated
FINAL CONSIDERATION: EXPECTED SUITABLE PACKAGING PROTOTYPE	

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Table 12. Applying the multicriteria roadmap to the nisin-PLA scenario of **Chapter 10**

Assessment of Packaging Evaluation Criteria	
Food preservation	Yes
Extend food shelf-life	Yes
Ensure food safety	Yes
Reduce wastes and losses	Yes, valorization of wheat straw residues and the co-product lactic acid to the production of the biofilm based on PLA
Meets market criteria	Yes
Preservation agents	Active packaging: Nisin
Assessment of Environmental Criteria	
Packaging material	Renewable and waste valorization resources
Biodegradability capacity	Yes
Environmental impacts	Reduced in comparison with common fossil-based food package due to the valorization and reduction of waste streams
Assessment of Circularity Criteria	
Degradability capacity	Yes, bio-based PLA
Recyclability capacity	Not evaluated but expected
Resource valorization	Yes: wheat straw
Use of waste streams	Yes: wheat straw
Reuse rate	Not evaluated
Assessment of Economic Criteria	
Financial metrics evaluation	Recovery of waste from renewable resources reduces the cost of raw materials compared to traditional plastic packaging.
Production process economy	Demonstrated
Life Cycle Cost	Economic metrics positive and adequate
Waste management costs	Reduced, due to the biodegradability and low toxicity of the packaging materials
Assessment of Social Criteria	
Consumer acceptance	Expected, as a biodegradable, environmentally friendly and functional food-packaging film is developed
Packaging design quality	Mechanical properties are ensured by the technological procedure followed
Brand communication	Not evaluated
FINAL CONSIDERATION: EXPECTED SUITABLE PACKAGING PROTOTYPE	

11.5 Discussion

Chapter 11 aimed to suggest the framework of multi-decision criteria for assessing the suitability of a bio-based food packaging prototype taking into account environmental, circular, economic and social concerns. On this basis, a preliminary literature review was conducted in order to identify the main trends and perspectives with respect to bio-based food packaging. By analyzing the main keywords selected from the research, five main criteria have been considered for the development of the multi-decision criteria diagram: Packaging Evaluation Criteria, Environmental Criteria, Circularity Criteria, Economic Criteria and Social Criteria. All the parameters encompassing each of the above criteria aim to provide an effective methodology for the assessment of the suitability of bio-based packaging products, being Life Cycle methodologies, the ones that are mandatory to be performed for a proper and comprehensive evaluation of the packaging prototype under assessment.

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SECTION VI.
Antioxidants

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SUMMARY

Antioxidants are substances capable of preventing, or scavenging, the damage caused to cells by free radicals, unstable molecular species that can cause harmful effects and accelerate chronic health problems such as inflammatory, cancer and cardiovascular diseases. Free radicals are natural by-products of human metabolism, the production of which can also be enhanced by environmental pollution and radiation. Given these issues, the application of antioxidants is essential in order to neutralize, or even break down, these free radicals to promote cell protection against oxidative stress and damage.

Many vegetables, fruits and nuts contain antioxidants in their molecular structure; however, their uptake depends on the bioavailability of the food source. For this reason, in recent years there has been an upward trend in the market chain of direct sales of antioxidant compounds as dietary supplements. For this purpose, it is necessary to extract the antioxidants from foods in which they are found in high concentrations or to promote their production through industrial biotechnology platforms. However, the latter option is not always economically viable, mainly because the use of commercial culture media is usually expensive and represent 25-40% of the total cost of the process. Therefore, considering the use of waste streams from industry and agri-food sectors as a potential source of antioxidants can be considered as an appropriate strategy, not only from an economic point of view, but also from the perspective of circularity, thus promoting a more efficient use and an added value to waste.

It is within this approach that the "**Section VI. Antioxidants**", where different schemes for the production of antioxidants from agricultural and food waste streams on an industrial scale are shown, including their environmental profiles, techno-economic and eco-efficiency analyses. To this end, **Chapter 12** is focused on the use of various antioxidant extraction technologies using beet waste as raw material, both more conventional technologies, such as Soxhlet, and more emerging ones, such as ultrasound or microwave. On the other hand, **Chapter 13** focuses on the production of resveratrol from food and forestry waste streams, in particular residues from wine production, cheese whey and eucalyptus.

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12

Bio-technological strategy to recover antioxidants from beet waste

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SUMMARY

The valorization of agro-industrial waste and residue streams for the recovery of high value-added compounds is a strategy that could be framed within circularity and sustainable management approaches. The rationale for this statement is twofold, not only for the reduction of waste streams to be managed, which implies impacts on environmental and economic aspects, but also for the recovery of a high-added and marketable product is obtained.

On the other hand, initiatives to improve sustainability should not only be based on increasing economic value, on enhancing the use of renewable resources, but also on promoting products that improve, or help to preserve, the health of consumers. In this context, antioxidants are classified as products with high added value, both because of their sale price (which is high) and because of their benefit to human health (against free radicals).

This is the framework in which **Chapter 12** is framed, since it promotes the valorization of beet waste for the extraction of antioxidants. Several extraction alternatives have been explored, including some more conventional (Soxhlet and maceration) and others more emerging, or in a lower degree of development (ultrasound, high pressurized liquid or supercritical fluid extraction). The comparison between them, and the selection of the best procedure, is possible with full-scale process modelling, environmental analysis through the application of LCA methodology and economic evaluation, together with sensitivity and eco-efficiency analyses.

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12.1 The bioactive potential of antioxidants

Vegetables are extraordinary sources of bioactive compounds and antioxidants. One of the predominant antioxidant compounds in vegetables, such as beets, are phenolics and betalains. The most abundant phenolic compound in beet is gallic acid, with anti-inflammatory, antioxidant and metabolic functions (Baião et al., 2020). However, other compounds may also be present: chlorogenic and syringic acids, quercetin, p-hydroxybenzoic and p-coumaric acids (Singh et al., 2019). As for betalains, their presence in beet is remarkable (Sigwela et al., 2021) and are considered one of the ten most potent natural antioxidants (Carrillo et al., 2017) and the most effective inhibitor of lipid peroxidation (Singh et al., 2019). In addition, betalains also have anticancer, antibacterial and anti-inflammatory properties, making them potential bioactive compounds (Fu et al., 2020).

The thermotolerance and thermodynamic stability of these compounds should be taken into account when developing a strategy for the extraction of antioxidant compounds from beet residues and side streams. Conventional extraction methods, such as Soxhlet and maceration, are widespread; however, in the search for new extraction technologies with better environmental profile, the so-called “Green Emerging Technologies” are proposed. In this manuscript, Ultrasound Assisted Extraction (UAE), Supercritical Fluid Extraction (SFE) and Pressurized Liquid Extraction (PLE) have been selected as green methods for the extraction of antioxidants, as both have shown promising results in terms of yield and productivity (Nirmal et al., 2021).

Despite the interest in the extraction and recovery of bioactive compounds and antioxidants from agricultural residues, most research has been conducted at laboratory scale. On the other hand, when looking for a new biotechnological route to be implemented, it is important to demonstrate its technical feasibility, as well as to estimate its environmental burdens, i.e., how this new approach could "help the environment" with the recovery and use of these waste streams, whether it could be considered as a sustainability approach and to what extent environmental burdens are reduced.

In this sense, the objective of this chapter is to model the processes for the extraction of antioxidants from beet residues, both leaves and stems, seeking to evaluate which of them has the highest yield and is the most environmentally friendly. For this purpose, a production capacity with an input of 100 kg/batch of beet waste was considered, using the SuperPro Designer tool. The results of the modeling phase will provide data for the LCA study, and, in addition, the operating costs of the entire production process have been taken into account.

12.2 Process description

One of the critical challenges in undertaking sustainable process design is the lack of full-scale process information. In response to this challenge, multi-criteria evaluation needs to be addressed at an early stage. It can be used to evaluate and support the decision-making process in process design, as well as to propose improvement actions. In this sense, ten antioxidant recovery scenarios have been proposed and modelled using the SuperPro Designer software, five of them for beet root residues and the rest for beet leaf residues. Regarding conventional extraction methods, the most widespread used Soxhlet and maceration have been simulated while for emerging technologies, UAE, SFE with CO_2 and PLE alternatives have been proposed (Lasta et al., 2019). For the development of the large-scale simulation, laboratory-scale literature data have been used, extrapolating the scenarios for 100 kg of beet waste per batch.

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The most important values considered for each of the extraction methodologies strategies are shown in **Table 1**.

Table 1. Main process conditions, yields and antioxidant capacities of the scenarios proposed (Lasta et al., 2019a; Lasta et al., 2019b)

Scenario	Process conditions	Yield and antioxidant capacity
So_L	Solvent: ethanol Ratio: 1:30 g: mL solvent Process time: 8 h Room temperature	Yield 21% w/w TPC:47 mg GAE/g extract EC50: 302 µg/mL TEAC: 586 µmol Trolox/ g extract PR: 182 µg/mL
So_S	Solvent: ethanol Ratio: 1:30 g: mL solvent Process time: 8 h Room temperature	Yield 9% w/w TPC: 55 mg GAE/g extract EC50: 59.4 g/mL TEAC: 730 µmol Trolox/ g extract PR: 63 µg/mL
M_L	Solvent: ethanol Ratio: 1:5 g: mL solvent Process time: 96 h Room temperature	Yield 1.6% w/w TPC: 21.3 mg GAE/g extract EC50: 139 g/mL TEAC: 254 µmol Trolox/ g extract PR: 259 µg/mL
M_S	Solvent: ethanol Ratio: 1:5 g: mL solvent Process time: 96 h Room temperature	Yield 5% w/w TPC: 22 mg GAE/g extract EC50: 518 g/mL TEAC: 11 µmol Trolox/ g extract PR: 163 µg/mL

Acronyms: L, beet leaves; S, beet stalk residues, So, Soxhlet extraction and M, maceration.

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Table 1. (cont.) Main process conditions, yields and antioxidant capacities of the scenarios proposed (Battistella Lasta et al., 2019; Lasta et al., 2019)

Scenario	Process conditions	Yield and antioxidant capacity
UAE_L	Solvent: ethanol Ratio: 1:30 g: mL solvent Process time: 7 min Room temperature 500 W sonication power	Yield 4.04% w/w TPC: 73 mg GAE/g extract EC50: 139 g/mL TEAC: 275 µmol Trolox/ g extract PR: 384 µg/mL
UAE_S	Solvent: ethanol Ratio: 1:30 g: mL solvent Process time: 7 min Room temperature 500 W sonication power	Yield 4.7% w/w TPC: 33 mg GAE/g extract EC50: 1147 g/mL TEAC: 83 µmol Trolox/ g extract PR: 30 µg/mL
SFE_L	Solvent: CO_2 +10% ethanol:water 0.5 kg CO_2/h Process time: 4 h 250 bar, 40 ºC	Yield 14.45% w/w TPC: 11 mg GAE/g extract EC50: 150 g/mL TEAC: 157 µmol Trolox/ g extract PR: 71 µg/mL
SFE_S	Solvent: CO_2 +10% ethanol:water 0.5 kg CO_2/h Process time: 4 h 250 bar, 40 ºC	Yield 6% w/w TPC: 23 mg GAE/g extract EC50: 738 g/mL TEAC: 137 µmol Trolox/ g extract PR: 70 µg/mL
PLE_L	Solvent: ethanol 3 mL/min Process time: 90 min 10 MPa, 40 ºC	Yield 12.3% w/w TPC: 252 mg GAE/g extract EC50: 65 g/mL TEAC: 400 µmol Trolox/ g extract PR: 275 µg/mL
PLE_S	Solvent: ethanol 3 mL/min Process time: 90 min 10 MPa, 40 ºC	Yield 9.9% w/w TPC: N/D EC50: 16 g/mL TEAC: 49.7 µmol Trolox/ g extract PR: 18 µg/mL

Acronyms: L, beet leaves; S, beet stalk residues, So, Soxhlet extraction and M, maceration.

The process scheme of Soxhlet, maceration, UAE and PLE are analogous: they are based on a tray drying to reduce the water content of the beet residues (**Figure 1**). Prior to extraction, it is necessary to cut the biomass to reduce its size. It is well known that the smaller the particle size, the higher the yield. In this stage, the operating conditions shown in **Table 1** have been considered. Once the residence time for the extraction has been reached, the separation of the biomass is performed using microfiltration equipment, followed by solvent recovery by multi-effect evaporation, and the final formulation of the extract using spray drying equipment to obtain a powder with a purity of 95%.

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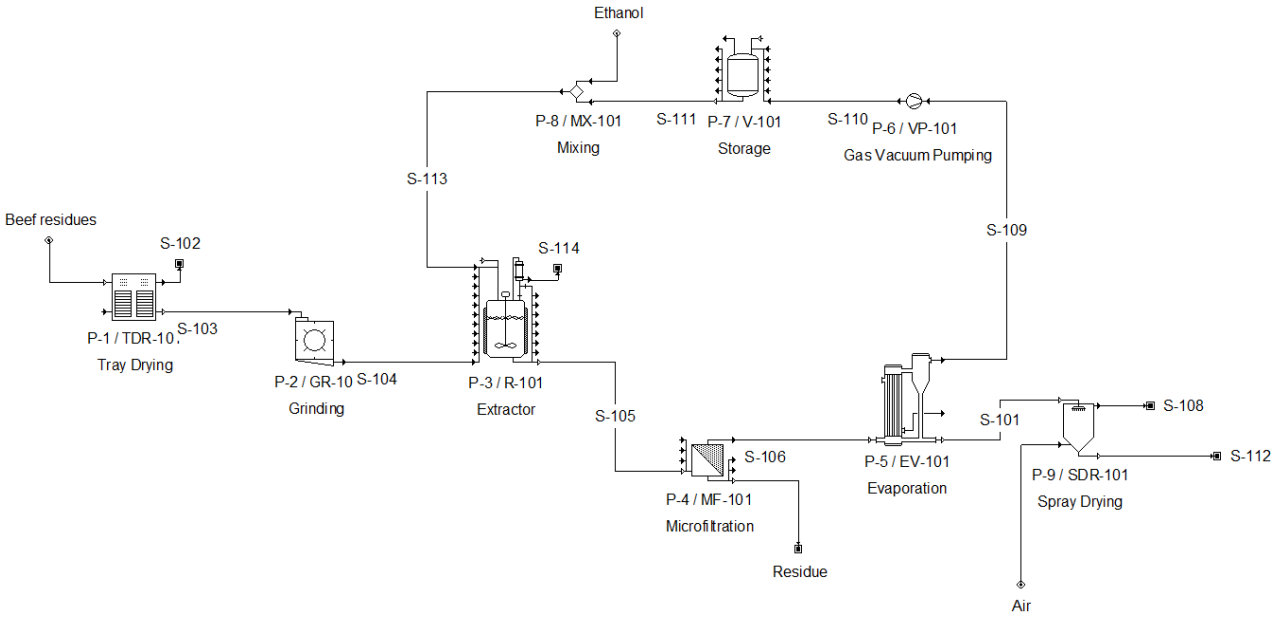

Figure 1. Soxhlet, maceration, UAE and PLE simulation with the SuperPro Designer software

Several differences can be distinguished in the simulation of the SFE scenarios (**Figure 2**). The extraction is based on the use of pressurized CO_2, which is subsequently recovered by flash evaporation. As for the last drying process, spray drying is not considered due to the low moisture content of the extract, so drum drying equipment is used.

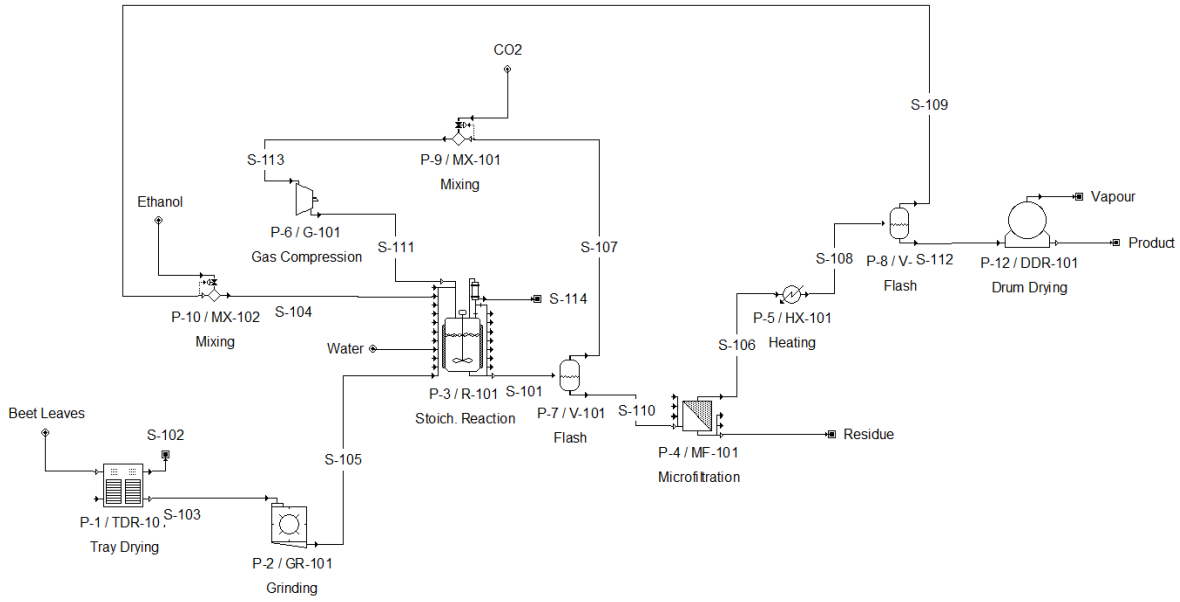

Figure 2. SFE simulation with the SuperPro Designer software

The amount of antioxidant produced depends on the yields and batch times required for each of the proposed extraction schemes. In this sense, the capacity and amount of product for each scenario are shown in **Table 2**. The detailed capacities of the process equipment are included in **Table 3.**

Table 2. Batch time, number of batches per year and antioxidant production capacity for each of the scenarios under assessment.

Scenario	Batch time (h)	Batches per year	Antioxidant production (kg/year)	Scenario	Batch time (h)	Batches per year	Antioxidant production (kg/year)
So_L	18.55	913	1620.51	**UAE_S**	11.12	1319	526.44
So_S	18.55	913	696.16	**SFE_L**	15.00	1318	1964.65
M_L	106.31	82	12.81	**SFE_S**	15.00	1318	818.55
M_S	106.31	82	39.77	**PLE_L**	12.50	1318	1397.96
UAE_L	11.12	1319	452.60	**PLE_S**	12.50	1318	1126.57

Table 3. Detailed capacity of process equipment.

Equipment	Capacity									
	S		M		UAE		SFE		PLE	
	L	S	L	S	L	S	L	S	L	S
Compressor (kW)	-	-	-	-	-	-	0.07	0.07	-	-
Drum Dryer (m^2)	-	-	-	-	-	-	0.02	0.02	-	-
Flash Drum (L)	-	-	-	-	-	-	1.80	0.33	-	-
Grinder (kg/h)	1.24	1.24	0.11	0.11	1.78	1.78	1.78	1.78	1.78	1.78
Microfilter (m^2)	3.13	3.15	0.59	0.59	3.16	3.16	0.03	0.02	1.90	1.90
Mixer (kg/h)	27.42	27.61	0.40	0.40	40.01	39.99	0.51	0.51	23.20	23.20
Multi-effect evaporator (m^2)	0.02	0.02	0.01	0.01	0.02	0.02	-	-	0.01	0.01
Tank (L)	256.8	259.4	49.5	49.5	260.4	260.3	-	-	157.9	158.3
Spray Dryer (L)	19.31	171.5	0.28	0.28	173.2	172.99	-	-	72.34	71.13
Extractor (L)	347.5	349.9	66.2	66.2	350.9	350.8	11.67	11.67	211.6	211.6
Tray dryer (m^2)	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	6.08
Vacuum pump (kW)	1.87	2.13	0.03	0.03	3.10	3.09	-	-	1.88	1.88

12.3 Applying LCA methodology

The LCA methodology was used to evaluate the environmental burdens of the extraction alternatives, with the objective of identifying the most environmentally promising valorization route. The data required for the life cycle inventories were obtained by simulating the process with the SuperPro Designer software. In order to improve the impact results, the main hotspots of the process were identified, with the development of the subsequent sensitivity analysis.

The functional unit (FU) selected for the evaluation has been the production of 1 g of antioxidant extract, with a purity of 95%, in line with other related studies for polyphenol extraction (Barjoveanu et al., 2020). The production capacity of the simulated facilities is identical for all scenarios: 100 kg beet residues/batch. As for the system boundaries, a "cradle to gate" approach has been considered, and regarding the calculation methodologies used to

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carry out the environmental profiles, the ReCiPe 2016 MidPoint and EndPoint methodologies have been selected to evaluate the midpoint and endpoint scores.

Mass and energy balance data related to the production process are presented in **Table 4** to **Table 13** and are estimated on the basis of 1 g of antioxidant-rich powder. The simulation of the production process has been developed according to laboratory data, so transport activities have not been taken into account within the environmental assessment, assuming that the process is delocalized. For the selection of the database, it is necessary to use one that provides all secondary data corresponding to the background activities of all inputs, such as solvent or beet residues, utilities (i.e., steam and cooling water), and waste streams such as spent biomass and the gas stream from the drying stages). In this regard, the Ecoinvent V3.2 database has been selected.

Table 4. LCI for scenario S_L: Soxhlet extraction using beet leaves residues.

INPUTS FROM TECHNOSPHERE			**OUTPUTS TO TECHNOSPHERE**		
Component	Amount	Unit	Component	Amount	Unit
Air	0.47	kg	Antioxidant	1	g
Beet Leaves	0.06	kg			
Solvent	0.03	kg	***Emissions***		
			Biomass	4.36	g
Energy requirements			Ethanol	33.19	g
Cooling Water	4.41	kg	Nitrogen	0.36	kg
Steam	0.12	kg	Oxygen	0.11	kg
Power	0.06	kWh	Water, vapor	50.73	g

Table 5. LCI for scenario S_S: Soxhlet extraction using beet stems residues.

INPUTS FROM TECHNOSPHERE			**OUTPUTS TO TECHNOSPHERE**		
Component	Amount	Unit	Component	Amount	Unit
Air	1.12	kg	Antioxidant	1	g
Beet Stems	0.13	kg			
Solvent	0.08	kg	***Emissions***		
			Biomass	11.68	g
Energy requirements			Ethanol	77.25	g
Cooling Water	10.26	kg	Nitrogen	0.86	kg
Steam	0.28	kg	Oxygen	0.26	kg
Power	0.07	kWh	Water, vapor	0.12	kg

Table 6. LCI for scenario M_L: Maceration extraction using beet leaves residues.

INPUTS FROM TECHNOSPHERE			**OUTPUTS TO TECHNOSPHERE**		
Component	Amount	Unit	Component	Amount	Unit
Air	0.87	kg	Antioxidant	1	g
Beet Leaves	0.64	kg			
Solvent	0.03	kg	***Emissions***		
			Biomass	12.63	g
Energy requirements			Ethanol	5.15	g
Cooling Water	9.87	kg	Nitrogen	0.14	kg
Steam	0.81	kg	Oxygen	0.04	kg
Power	0.05	kWh	Water, vapor	0.12	kg

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Table 7. LCI for scenario M_S: Maceration extraction using beet stems residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Air	0.28	kg	Antioxidant	1	g
Beet Stems	0.21	kg			
Solvent	0.01	kg	***Emissions***		
			Biomass	12.19	g
Energy requirements			Ethanol	5.50	g
Cooling Water	3.15	kg	Nitrogen	0.14	kg
Steam	0.26	kg	Oxygen	0.04	kg
Power	0.05	kWh	Water, vapor	0.12	kg

Table 8. LCI for scenario UAE_L: Ultrasound assisted extraction using beet leaves residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Air	2.52	kg	Antioxidant	1	g
Beet Leaves	0.29	kg			
Solvent	0.17	kg	***Emissions***		
			Biomass	27.41	g
Energy requirements			Ethanol	0.15	kg
Cooling Water	53.72	kg	Nitrogen	1.94	kg
Steam	0.62	kg	Oxygen	0.59	kg
Power	1.29	kWh	Water, vapor	0.26	kg

Table 9. LCI for scenario UAE_S: Ultrasound assisted extraction using beet stems residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Air	2.17	kg	Antioxidant	1	g
Beet Stems	0.25	kg			
Solvent	0.15	kg	***Emissions***		
			Biomass	23.40	g
Energy requirements			Ethanol	0.13	kg
Cooling Water	62.33	kg	Nitrogen	1.66	kg
Steam	0.53	kg	Oxygen	0.50	kg
Power	1.29	kWh	Water, vapor	0.23	kg

Table 10. LCI for scenario PLE_L: Pressurized liquid extraction using beet leaves residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Air	0.34	kg	Antioxidant	1	g
Beet Leaves	0.09	kg			
Solvent	0.03	kg			
			Emissions		
			Biomass	8.10	g
Energy requirements			Ethanol	0.03	kg
Cooling Water	4.50	kg	Nitrogen	0.26	kg
Steam	0.16	kg	Oxygen	0.08	kg
Power	0.10	kWh	Water, vapor	0.08	kg

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Table 11. LCI for scenario PLE_S: Pressurized liquid extraction using beet stems residues

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Air	0.42	kg	Antioxidant	1	g
Beet Stems	0.12	kg			
Solvent	0.03	kg			
			Emissions		
			Biomass	10.33	g
Energy requirements			Ethanol	0.03	kg
Cooling Water	5.61	kg	Nitrogen	0.32	kg
Steam	0.20	kg	Oxygen	0.09	kg
Power	0.10	kWh	Water, vapor	0.11	kg

Table 12. LCI for scenario SFE_L: Supercritical fluid extraction using beet leaves residues

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Beet Leaves	0.07	kg	Antioxidant	1	g
Ethanol:Water	0.01	g			
Energy requirements					
Cooling Water	0.05	kg	***Emissions***		
Steam	0.07	kg	Biomass	5.63	g
Power	0.10	kWh	Water, vapor	0.06	kg

Table 13. LCI for scenario SFE_S: Supercritical fluid extraction using beet stems residues

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Component	Amount	Unit	Component	Amount	Unit
Beet Stems	0.09	kg	Antioxidant	1	g
Ethanol:Water	0.03	g			
Energy requirements					
Cooling Water	0.11	kg	***Emissions***		
Steam	0.18	kg	Biomass	14.83	g
Power	0.10	kWh	Water, vapor	0.15	kg

On the other hand, in order to improve the environmental profiles and impact results obtained for the proposed scenarios, sensitivity analyses will be performed for the main hotspots identified. For scenarios in which energy requirements are the main hotspots, the use of renewable resources will be proposed, for those in which the solvent is one of the main contributors to the environmental profile, the use of other efficient extractants will be evaluated, as is the case of the ethanol:water mixture or hexane (Chemat et al., 2020).

12.4 Evaluation scenarios under an environmental perspective

In order to evaluate which of the extraction procedures is the best alternative from an environmental point of view, an analysis of the profiles obtained for each of the proposed scenarios was carried out. With this evaluation, it has been possible to identify the main contributors to the impact values, where improvement actions should be considered to reduce environmental impacts.

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12.4.1 Environmental profile of Soxhlet extraction scenarios

Figure 3 illustrates the environmental profile of antioxidant production from leaf and stem residues, applying Soxhlet extraction technology. The acronyms L and S represent leaves and stems, respectively. As can be observed, the difference between using leaves or stems as input resources is not so significant, since this variation depends directly on the extraction yield value, without any other difference in the process scheme.

In the environmental profile, it has been possible to identify three main hotspots. The one that stands out the most is electricity, being the major contributor in the impact categories related to eutrophication (FE and ME), and toxicity (FET, MET and TET), while in the case of the TET, FRS and GW categories it is the solvent used: ethanol, that entails the greatest impact. In the case of steam requirements, it ranks third, with the largest contribution in the TET and FRS impact categories.

On the other hand, the environmental contribution of beet waste in the TET impact category is remarkable. The negative value can be considered as an environmental credit and is justified on the basis of the strategy of valorization of beet waste as a resource to produce antioxidants, which avoids the equivalent external process to produce a similar amount of the target product.

Process emissions have their environmental contribution in the OP category, with a value close to 100%, which is attributed to ethanol emissions. Although the negative impact of VOCs on the atmosphere is well-known, it is important to mention that ethanol is classified as a category B compound, indicating a low hazard.

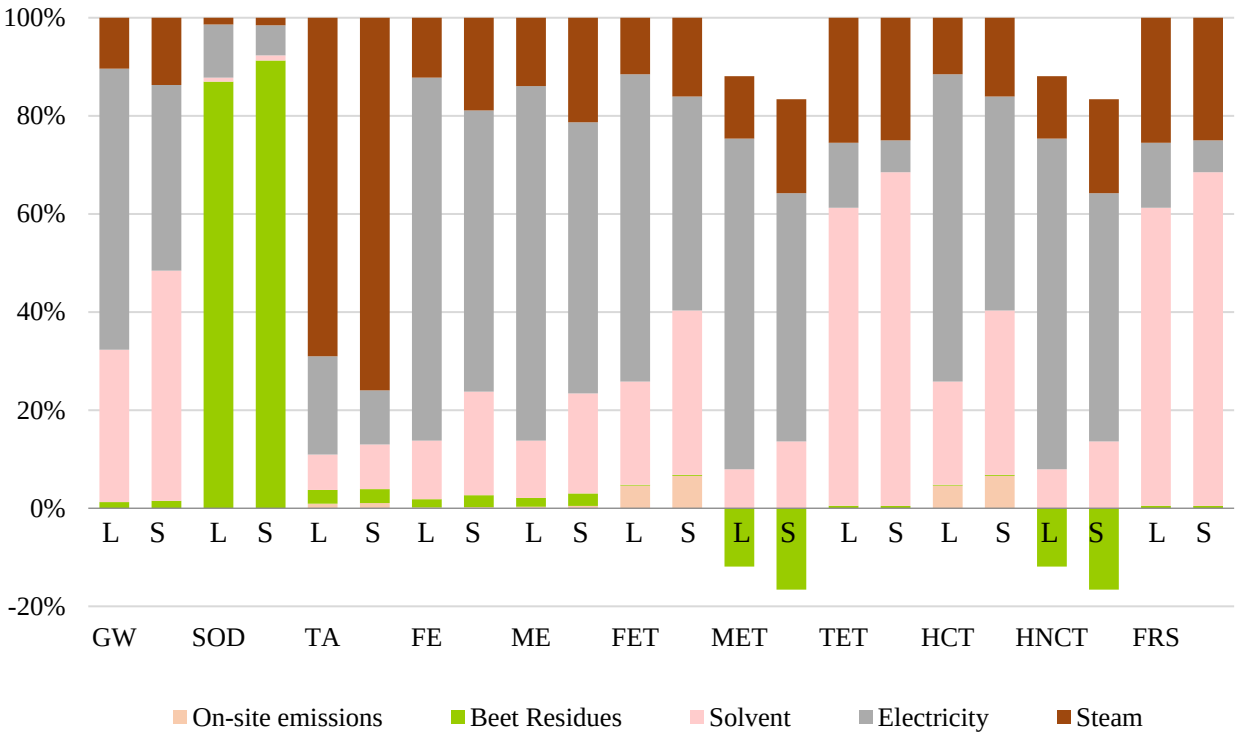

Figure 3. Environmental impacts of Soxhlet extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

12.4.2 Environmental profile of the maceration extraction scenarios

The environmental results of the maceration extraction scenarios are shown in **Figure 4**. As observed for Soxhlet extraction, the use of leaves or stems does not imply significant

contribution differences in the environmental profile. However, there are significant differences in terms of energy needs; while in the Soxhlet scenario electricity was the main hotspot, in the Maceration scenario steam requirements stands out the most.

The use of steam produced from renewable resources could be considered, as it is observed that GWP, TA and TET are the most affected categories, which is directly related to the use of fossil fuels and CO_2 emissions. To improve the profile, it would be desirable to use steam produced from renewable resources, so this option will be taken into account in the sensitivity assessment.

As observed in **Figure 4**, the solvent contribution is not as significant as in the Soxhlet one. The reason is based on the solute:solvent ratio required for the maceration extraction: 1:5, much lower than that of Soxhlet: 1:30. This lower solvent consumption leads to a minor contribution to the environmental profile.

On the other hand, as far as beet residues are concerned, their contribution is higher in the SOD category. This can be explained in terms of the yield value, which is much lower compared to Soxhlet extraction, meaning that, to produce the same amount of antioxidant: 1 g, a higher amount of beet waste is required, so its contribution to the environmental profile will also be higher. Consequently, production capacity and overall process yield are key factors in the selection of the most environmentally sound alternative.

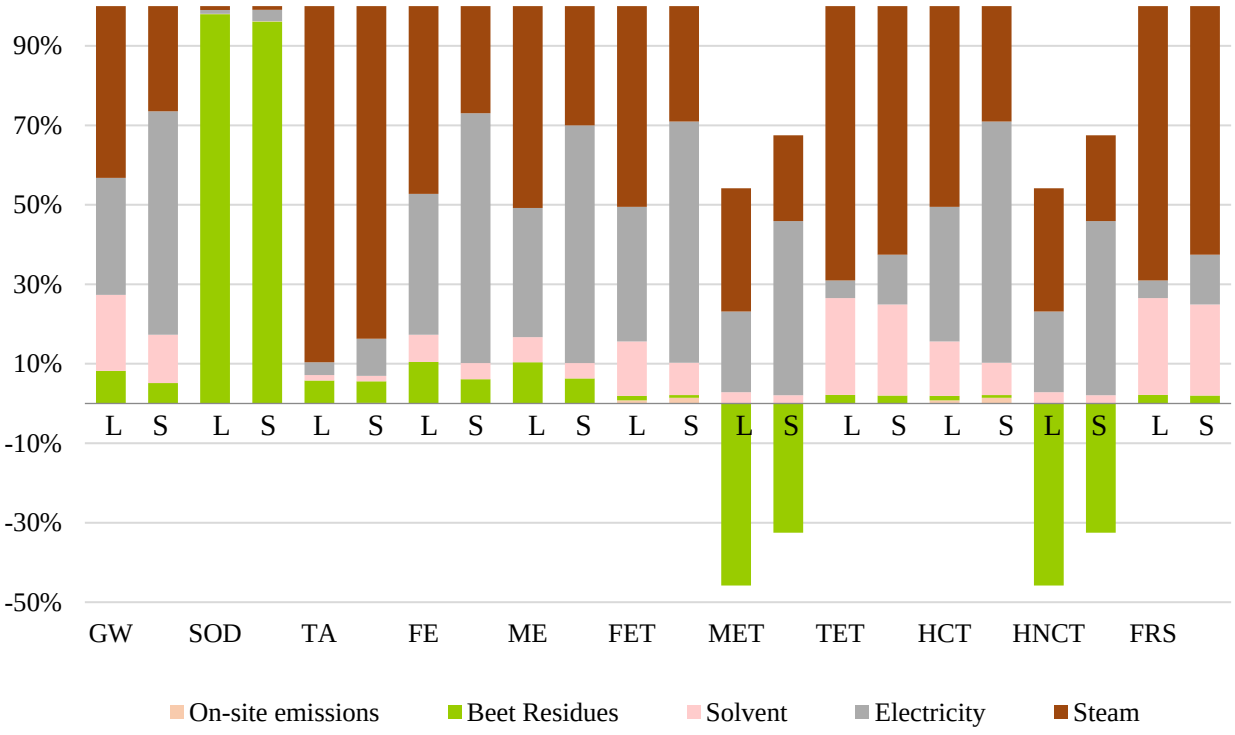

Figure 4. Environmental impacts of the maceration extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

12.4.3 Environmental profile of the UAE extraction scenarios

The outcomes of the UAE process do not provide the highest yields (**Table 1**), but as for the PLE process, it entails the best antioxidant results in terms of TPC, TEAC and PR values. The EC_{50} value, which represents the effective concentration of the extract to reach 50% of the antioxidant potential, should be as low as possible for a better antioxidant potential, and

reasonably small values are obtained when developing the UAE technology. Another fact to consider is the extraction time of the UAE process, only 7 minutes are needed for the extraction of the antioxidant compounds, which increases the annual capacity of the plant.

The environmental profile of the UAE scenarios developed for leaves and stems is illustrated in **Figure 5**. As expected, it is the impact of electricity requirements that stands out, mainly in all impact categories, as UAE is a highly energy demanding technology. The best way to reduce its impact would be to apply renewable resources to produce electricity, instead of using fossil resources. In addition to electricity, the impact on the use of solvents is also noticeable in the SOD category. The reason for this contribution to the impact is the result of the background activities associated with solvent production, which is based on the use of fossil resources and non-renewable materials.

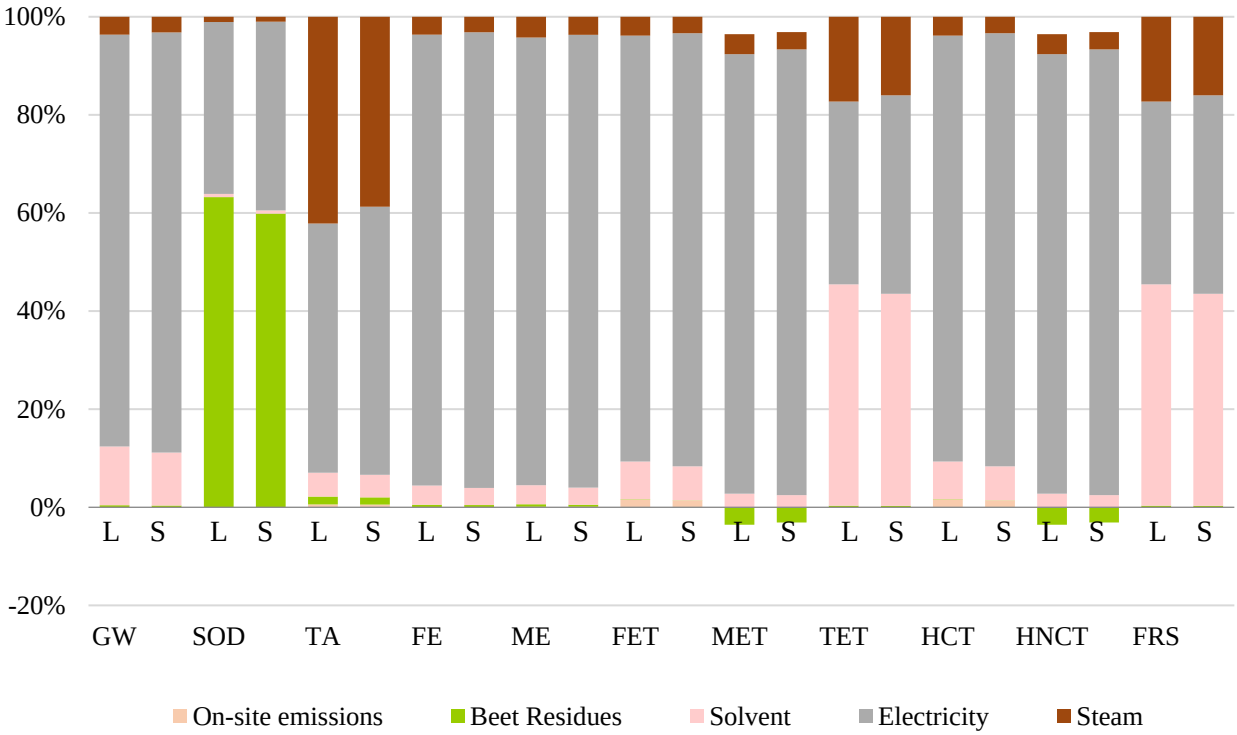

Figure 5. Environmental impacts of UAE extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

12.4.4 Environmental profile of SFE extraction scenarios

Carbon dioxide, together with ethanol and water, is the main solvent used in SFE, which requires 250 bar and 4 h. As in previous profiles, the contribution of electricity requirements remains important, being the main hotspot in most impact categories, except for TA, TET and FRS, where the contribution of steam is also significant (**Figure 6**).

Comparing the SFE environmental profile with the previous ones assessed, two main differences can be identified. First, the lack of emissions impact, due to the use of CO_2 as the main solvent, which is mostly recycled to the process, avoiding on-site emissions from the process and solvent inputs. Secondly, as the amount of ethanol used in the SFE is very low, the output of ethanol in the waste and secondary streams is also small, which implies that the environmental contribution of these flows is not substantial.

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On the other hand, it is also observed that, when comparing the environmental contribution of the components when leaves or stems are used as the main input, the differences are greater than in the previous scenarios. This fact could be explained by the yield results obtained for each of them, while the yield for leaves amounts to 14.45%, the values decrease to 6% for stems.

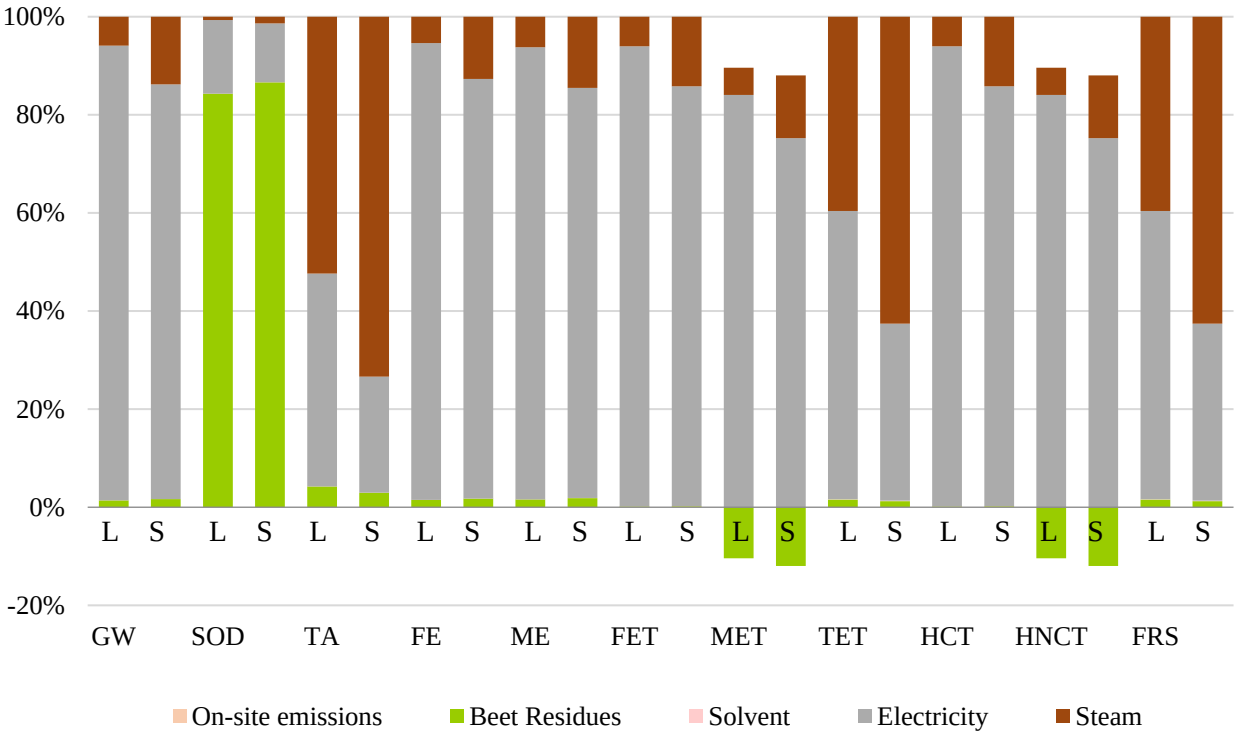

Figure 6. Environmental impacts of SFE extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

12.4.5 Environmental profile of PLE extraction scenarios

When selecting an extraction alternative, it is not only the environmental profile that must be taken into account, but also the characteristics of the target product, in this case, its properties and antioxidant capacity. It is in the case of PLE where the best values of antioxidant capacity of the extracted product are obtained, according to the data included in **Tables 1**. In this case, the environmental contribution of the solvent, ethanol with a flow rate of 9 mL/min, is noticeable in mainly all the impact categories, being TET and FRS the most relevant (**Figure 7**). The fact that this chemical compound is produced using fossil resources and non-renewable compounds is the main reason for this contribution. One possibility to reduce its environmental impact would be related to the use of bioethanol produced from renewable resources.

Considering the operation conditions of 40º C, 10 MPa and 90 min, energy represents the greatest environmental contribution. In the case of TA, the use of steam as a heat source has the largest influence, corresponding to approximately 50% of the total impact. The use of beet residues to produce antioxidants leads to environmental benefits in the MET and HTNC impact category, reducing the impact by approximately 15%. To achieve a better environmental profile, with a lower contribution of electricity consumption, it would be desirable to optimize the extraction process and reduce the residence time, as well as to use renewable energy sources.

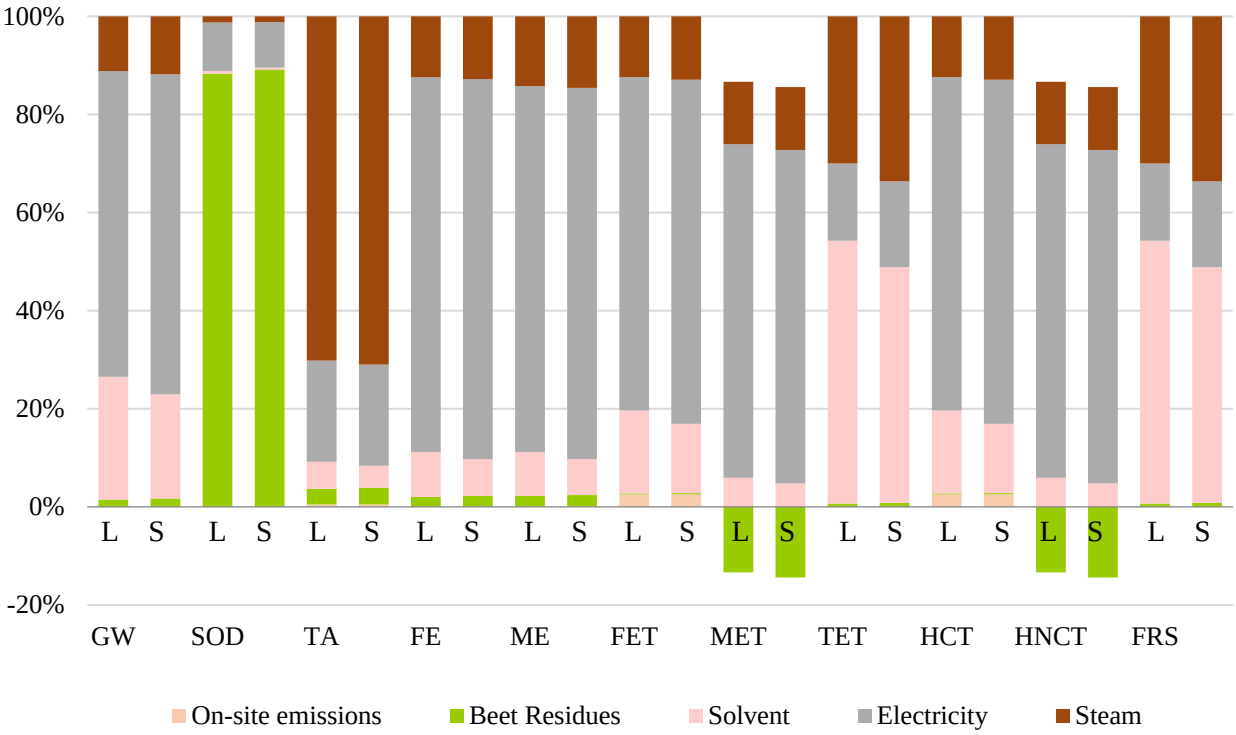

Figure 7. Environmental impacts of PLE extraction expressed as mid-point impact categories. Acronyms: Beet leaves (L), beet stems (S).

12.5 Economic evaluation

With the aim of evaluating the technical and economic feasibility, a techno-economic evaluation of the beet waste valorization alternatives has been proposed. This evaluation involves an exhaustive analysis of the process scheme by integrating engineering and economic aspects. With the economic scores it was possible to select the most appropriate scenario in terms of profitability and efficiency of the process.

Regarding the economic viability, the minimum selling prices of the antioxidant obtained are calculated based on the associated capital costs, the operating costs and the estimated revenues generated by the sale of the antioxidants produced. It is worth mentioning that these costs are estimated based on the identified process steps, conversion technologies, production capacity and equipment characteristics, such as reactor volume, drying capacity, filtration capacity, etc. Capital costs have been calculated from the cost of equipment, which has been estimated according to the information available in the tabulated data of Smith and Sinnot, taking into account the data estimated by the SuperPro Designer tool (Smith, 2005; Towler and Sinnott, 2021). With respect to the operating costs, those are assumed mainly on the raw materials costs, utilities costs, labor costs and equipment maintenance expenses. On the other hand, the main assumptions on the performance of the techno-economic assessment have been based on the recent research report developed by Adeyi et al. (2022), which has evaluated the production-scale process of bioactive extracts from *Senna alata* leaves, using "heat assisted extraction" as the extraction method (Adeyi et al., 2022).

With this in mind, **Table 14** is depicted, which includes all the economic parameters related to the 8 process scenarios evaluated. As can be seen, there are significant variations in some of

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the parameters included, for example, in the case of total investment, the development of the SFE extraction method implies the largest amount, followed by the UAE alternative. This could be expected given that these technologies are at an early stage of large-scale design, leading to higher investment costs. A similar trend is observed for equipment costs, with these two alternatives having the highest associated cost, based on the same reason. However, when evaluating the minimum selling price of the antioxidant produced, the scores obtained are higher than conventional extraction technology, maceration and Soxhlet, which is to be expected given the lower annual production capacity of the antioxidant. The reason behind this lies in the processing time required, the extraction time of maceration is significantly longer than that of SFE, PLE or UAE, which implies that less amount of antioxidant is produced, given the reduced amount of batch processing that could be developed annually. However, an exception can be observed for the UAE extraction methodology, whose minimum selling prices are slightly higher compared to Soxhlet, given the lower amount of antioxidant that can be extracted compared to conventional technology, as shown in **Table 2.** In this case, the advantage of selecting UAE throughput to achieve greater cost-effectiveness when assessing economic performance.

Finally, in terms of revenue, emerging technologies are the ones that achieve higher ones, together with the Soxhlet extraction method. Overall, it could be concluded that SFE and PLE development are the most economically attractive emerging technologies, given the scores obtained for minimum selling prices and expected revenues, and the Soxhlet alternative as the best for conventional ones, with even better economic scores compared to the UAE alternative.

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Table 14. Economic parameters obtained by performing the economic evaluation of the biotechnological production process of antioxidants from beet wastes.

Economic Parameters	M_L	M_S	PLE_L	PLE_S	S_S
Total Investment [€]	1,063,000	1,063,000	1,135,000	2,395,000	5,136,000
Equipment cost [€]	215,000	215,000	223,000	339,000	781,000
Fixed Capital [€]	937,000	937,000	974,000	2,078,000	4,693,000
1. Total Plant Direct Cost [€]	582,000	582,000	605,000	1,129,000	2,551,000
2. Total Plant Indirect Cost [€]	233,000	233,000	242,000	678,000	1,530,000
Labor Cost [€/year]	937,000	937,000	974,000	2,078,000	4,693,000
Annual Operation Cost [€/year]	983,000	983,000	1,361,000	3,085,000	3,175,000
Revenues [€/year]	1,462,687	471,145	41,446,669	54,143,094	26,955,332
MSP [€/g]	26.01	80.77	1.27	2.32	4.80
Economic Parameters	**S_L**	**SFE_S**	**SFE_L**	**UAE_L**	**UAE_S**
Total Investment [€]	5,151,000	4,532,000	4,516,000	2,962,000	2,578,000
Equipment cost [€]	779,000	688,000	688,000	438,000	379,000
Fixed Capital [€]	4,686,000	4,143,000	4,147,000	2,681,000	2,316,000
1. Total Plant Direct Cost [€]	2,547,000	2,252,000	2,254,000	1,457,000	1,259,000
2. Total Plant Indirect Cost [€]	1,528,000	1,351,000	1,352,000	874,000	755,000
Labor Cost [€/year]	4,686,000	4,143,000	4,147,000	2,681,000	2,316,000
Annual Operation Cost [€/year]	3,420,000	3,078,000	2,814,000	2,353,000	2,279,000
Revenues [€/year]	59,602,359	31,678,286	76,033,256	12,737,428	10,950,842
MSP [€/g]	2.22	3.76	1.43	7.15	8.06

12.6 Comparison between scenarios

To identify the best alternative for the valorization of beet wastes as inputs for antioxidant extraction, several aspects will be considered: antioxidant recovery yields, production capacity and environmental impacts. The PLE technology is the one that obtains the best antioxidant capacity values, reaching a value of 65 and 16 g/L for leaves and stems, respectively. It is also with this extraction method that, together with SFE and Soxhlet, the highest production capacity is achieved, with more than 1000 kg/year of antioxidant. In terms of environmental values, there is one technology that could be identified as having the greatest contribution to environmental impact (**Table 15**): UAE. While in terms of production and antioxidant capacities the results are promising, the high energy demand of the extraction process implies a significant environmental impact and improvements are needed to reduce it.

Although no major differences are observed when comparing the rest of the alternative extraction process scenarios, two of them can be identified as having the lowest environmental impact and, therefore, can be considered the most efficient in environmental terms. This is the case of SFE and PLE technologies, whose impact values are quite similar, although certain differences are observed. The most significant variations are observed in the TA impact category, where the impact value of SFE is 1.53 times and 1.35 times higher for leaves and stems respectively, in TET, where the impact of the PLE scenario is 1.20 and 1.30 times more impactful compared to that of SFE, and in the ME category, again the PLE scenario is the one with the highest environmental load, at an average value of 1.26 times (**Table 15**).

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Table 15. Characterization values of the scenarios assessed for the extraction of the antioxidant compounds from beet residues valorization.

Impact category	Unit	M_L	M_S	PLE_L	PLE_S	S_L
GW	kg CO_2 eq	0.31	0.11	0.11	0.13	0.09
SOD	kg CFC_{11} eq	$7.05 \cdot 10^{-7}$	$2.37 \cdot 10^{-7}$	$1.18 \cdot 10^{-7}$	$1.54 \cdot 10^{-7}$	$8.11 \cdot 10^{-8}$
TA	kg SO_2 eq	$9.65 \cdot 10^{-4}$	$3.60 \cdot 10^{-4}$	$3.33 \cdot 10^{-4}$	$4.00 \cdot 10^{-4}$	$2.64 \cdot 10^{-4}$
FE	kg P eq	$6.64 \cdot 10^{-5}$	$3.48 \cdot 10^{-5}$	$5.08 \cdot 10^{-5}$	$5.99 \cdot 10^{-5}$	$4.09 \cdot 10^{-5}$
ME	kg N eq	$1.44 \cdot 10^{-4}$	$4.82 \cdot 10^{-5}$	$2.25 \cdot 10^{-5}$	$2.97 \cdot 10^{-5}$	$1.52 \cdot 10^{-5}$
TET	kg 1.4-DCB	0.36	0.12	0.09	0.11	0.07
FET	kg 1.4-DCB	$1.42 \cdot 10^{-3}$	$8.01 \cdot 10^{-4}$	$1.07 \cdot 10^{-3}$	$1.30 \cdot 10^{-3}$	$8.16 \cdot 10^{-4}$
MET	kg 1.4-DCB	$2.15 \cdot 10^{-3}$	$1.17 \cdot 10^{-3}$	$1.52 \cdot 10^{-3}$	$1.85 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$
HCT	kg 1.4-DCB	$3.03 \cdot 10^{-3}$	$1.69 \cdot 10^{-3}$	$2.44 \cdot 10^{-3}$	$2.92 \cdot 10^{-3}$	$1.97 \cdot 10^{-3}$
HNCT	kg 1.4-DCB	0.01	0.02	0.04	0.05	0.03
FRS	kg oil eq	0.12	0.04	0.05	0.06	0.05
Impact category	**Unit**	**S_S**	**SFE_L**	**SFE_S**	**UAE_L**	**UAE_S**
GW	kg CO_2 eq	0.20	0.06	0.09	0.88	0.83
SOD	kg CFC_{11} eq	$1.67 \cdot 10^{-7}$	$9.30 \cdot 10^{-8}$	$1.21 \cdot 10^{-7}$	$5.81 \cdot 10^{-7}$	$5.33 \cdot 10^{-7}$
TA	kg SO_2 eq	$5.39 \cdot 10^{-4}$	$2.18 \cdot 10^{-4}$	$2.97 \cdot 10^{-4}$	$2.76 \cdot 10^{-3}$	$2.64 \cdot 10^{-3}$
FE	kg P eq	$7.23 \cdot 10^{-5}$	$4.22 \cdot 10^{-5}$	$4.62 \cdot 10^{-5}$	$6.00 \cdot 10^{-4}$	$5.88 \cdot 10^{-4}$
ME	kg N eq	$3.14 \cdot 10^{-5}$	$1.83 \cdot 10^{-5}$	$2.29 \cdot 10^{-5}$	$1.01 \cdot 10^{-4}$	$9.22 \cdot 10^{-5}$
TET	kg 1.4-DCB	0.15	0.05	0.10	0.58	0.54
FET	kg 1.4-DCB	$1.23 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$	0.01	0.01
MET	kg 1.4-DCB	$1.77 \cdot 10^{-3}$	$1.52 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$	0.02	0.02
HCT	kg 1.4-DCB	$3.29 \cdot 10^{-3}$	$2.19 \cdot 10^{-3}$	$2.40 \cdot 10^{-3}$	0.03	0.03
HNCT	kg 1.4-DCB	0.04	0.04	0.05	0.62	0.62
FRS	kg oil eq	0.11	0.02	0.03	0.36	0.33

On the other hand, to provide another comparison between the alternatives, but in a more condensed form, the ReCiPe EndPoint methodology has been used, as it allows obtaining a single score value that encompasses three main categories of damage to human health and ecosystems and depletion of fossil resources (**Figure 8**).

As previously obtained, the UAE scenarios have the highest environmental single score value, significantly higher compared to the other extraction technologies, with percentage of increased value between 72% and 93%. On the other hand, certain differences could be identified when comparing leaves and stems as renewable resources for the extraction of antioxidant compounds, being the use of stems the one with the highest environmental impact in all the proposed scenarios, except for the maceration and UAE scenarios, where the use of leaves supposes the highest impact, this difference being more significant for the maceration alternative. Looking for the best extraction alternative, both SFE and PLE could be defined as the most promising, since their environmental impact values are the lowest.

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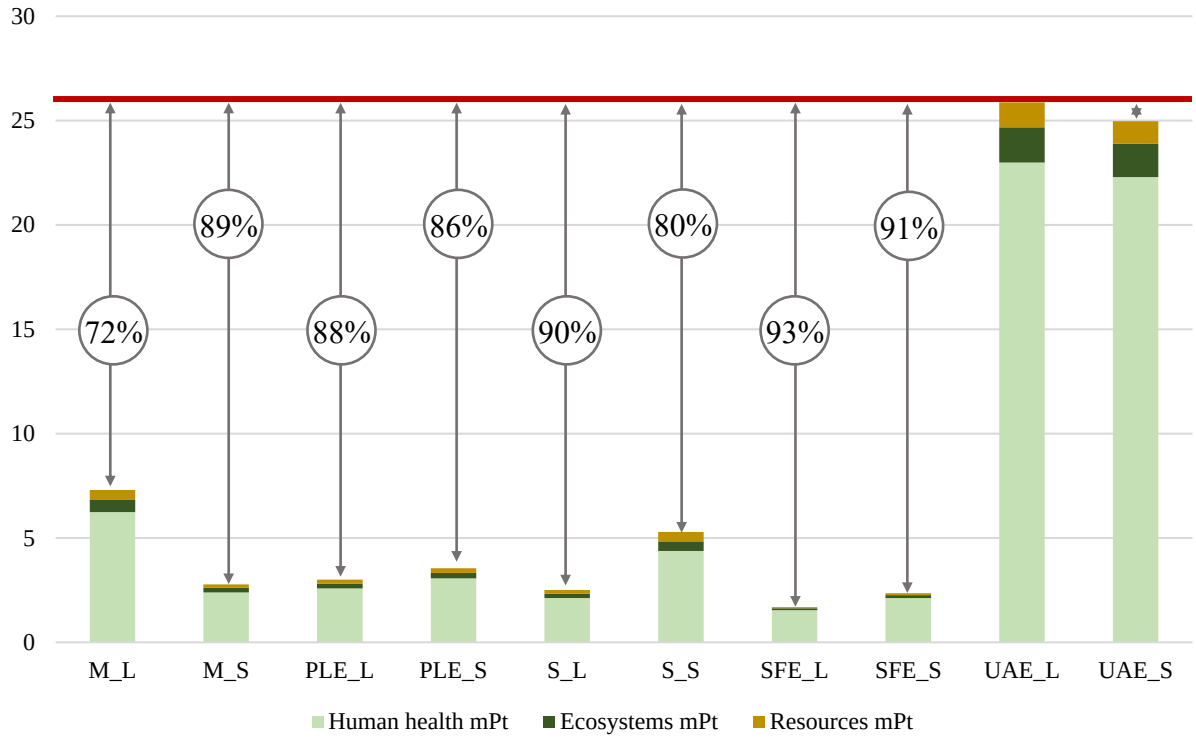

Figure 8. EndPoint score values obtained for the assessed scenarios

12.7 Sensitivity analysis to improve the environmental profiles

In order to improve the environmental profiles of the presented scenarios, sensitivity analyses have been performed focusing on the main critical points identified for each of the evaluated alternatives. As the main hot spot is electricity, the substitution of fossil resources by hydropower is an option to be considered. To evaluate the improvements of the sensitivity scenarios, the normalization values of the ReCiPe MidPoint methodology have been used, obtaining a score that is the result of the sum of all the impact categories that were included in the baseline environmental profiles (**Figure 9**). The best results were obtained for the SFE and UAE technologies, as expected, since they have the highest electricity demand. However, significant improvements were also obtained for the other scenarios, with reduction values between 26% and 64%.

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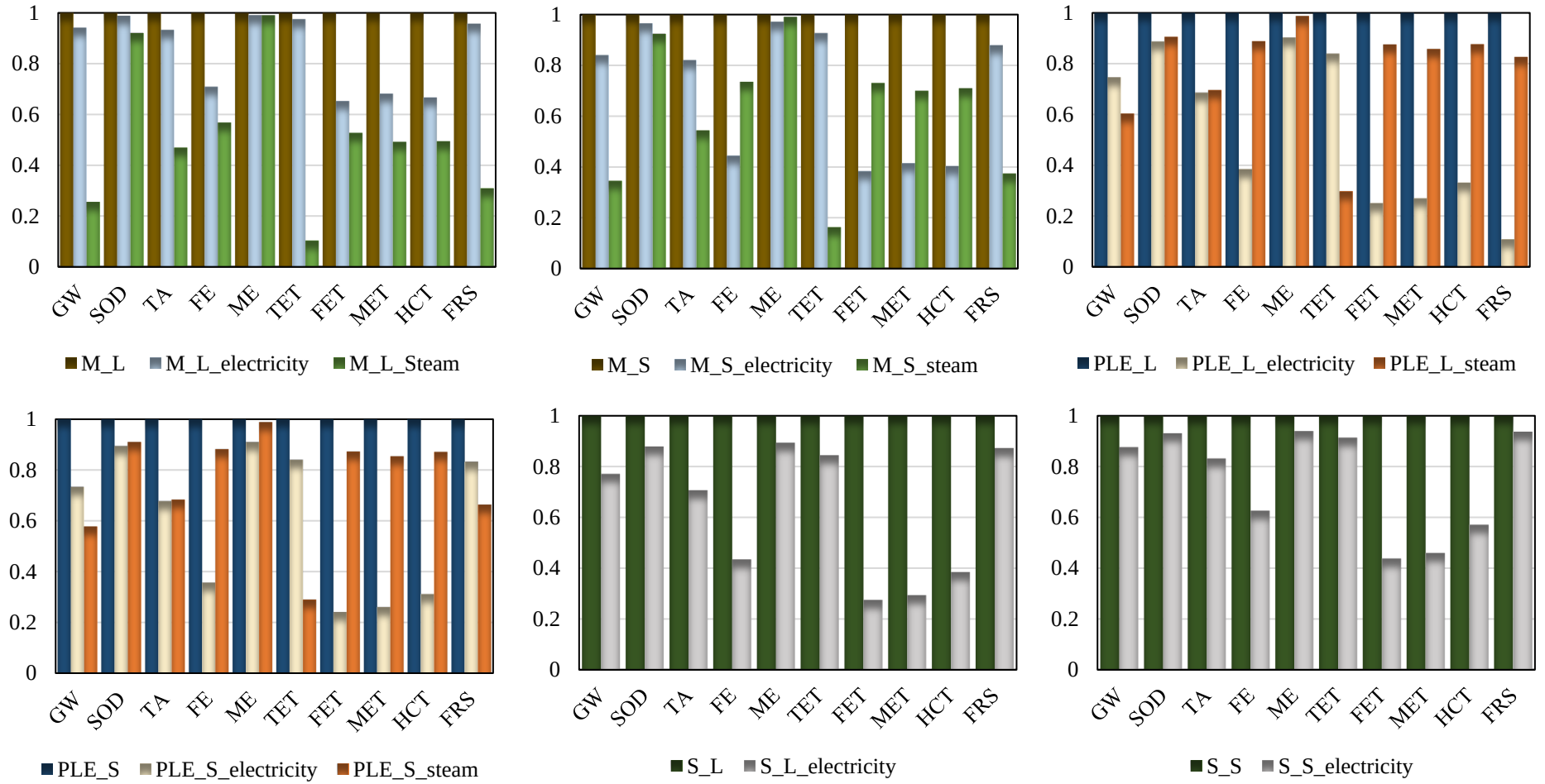

Figure 9. Sensitivity assessments to achieve improved environmental profiles for the maceration (M_L and M_S), pressurized liquid extraction (PLE_L and PLE_S) and Soxhlet (S_L and S_S) extraction alternatives.

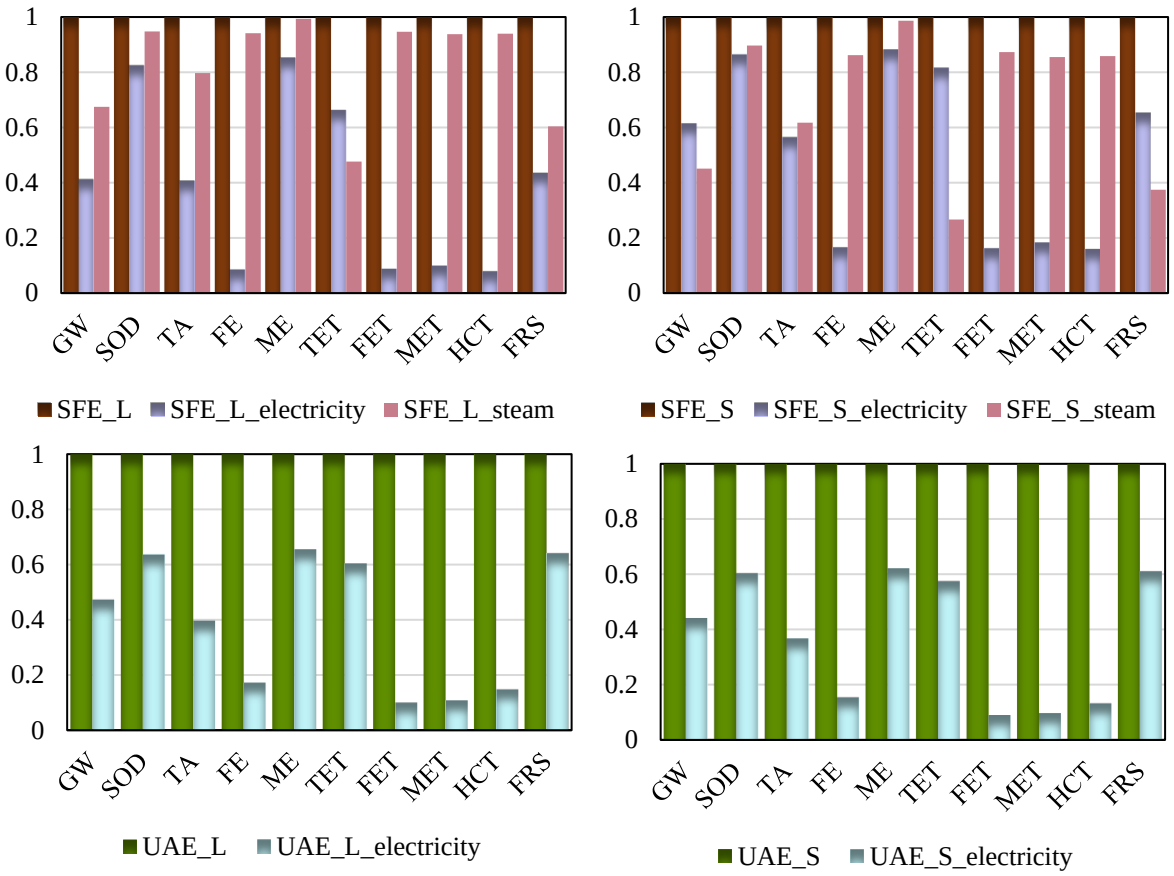

Figure 10. Sensitivity assessments to achieve improved environmental profiles for the supercritical fluid extraction (SFE_L and SFE_S) and Ultrasound Assisted Extraction (UAE_L and UAE_S) alternatives.

For the conventional extraction technology of maceration, two main sensitivity scenarios have been proposed, reductions in electricity use and steam requirements by 25% each (**Figure 9**). The results on environmental load diminishment obtained are significantly promising, acquiring higher reduction values for the reduction in steam requirements in this case. On the other hand, when comparing between the fraction of stems and leaves, it is appreciated that, for some impact categories, the values obtained for electricity reduction are smaller, for the fraction of stems, for the impact categories of FE, FET, MET and HCT. Besides, in the case of GW and FRS, the reduction values obtained for this valorization scenario are higher, approximately a reduction of 10%.

With respect to the PLE alternative, an analogous result is observed between the use of stems and leaves, being the reduction of steam needs what leads to a greater reduction of the impact in the GW and TET categories, while a lower use of electricity implies a more significant reduction of environmental damage in the rest of the categories (**Figure 9**). The categories associated with ecotoxicity and consumption of fossil resources show the greatest reduction in impact, reaching values between 70% and 90%. However, it is important to mention that these scores were to be expected, given that this technology requires high pressure and temperature, which implies a large energy requirement.

In the case of the Soxhlet alternative, it has been decided to evaluate how the reduction of electricity affects the potential environmental impact, since this is the main hotspot identified in the environmental profile shown in **Figure 3**. As can be seen in **Figure 9**, significant impact

reductions are achieved in all the categories under evaluation, with the most notable improvement in the FET, MET, HCT and FRS categories. Overall, the impact reduction value amounts to 44%, with a range between 11% achieved for the ME category and 85% obtained for FRS, in the case of leaf valorization. For extraction from stems, the average value achieved is somewhat lower, 31%, with a range between 6% for the ME impact category and 73% for FRS.

Regarding the two remaining alternatives, for the recovery of leaves with the SFE technology, the reduction of electricity needs is the one that leads to the highest degree of improvement in most of the impact categories, with the exception of the TET category. Thus, taking the initiative towards a diminishment of steam requirements implies a further reduction of the environmental impact, approximately 10% (**Figure 10**). On the other hand, the impact categories with the best decreasing values are those associated with FE, FET, MET, HCT and FRS, between 80-90% impact reduction. When the stems are used as input for the extraction process, certain differences are observed between the environmental outcomes when compared to the use of leaves. The reduction in the use of steam acquires better reduction values, not only in the TET category, as in the previous case, but also in the GW category, again 10% higher. For the remaining categories, it is still the reduction in the use of electricity that leads to an overall improvement in the profile, with the FE, FET, MET, HCT and FRS categories again showing the greatest improvements in their environmental profile. On the other hand, it should be noted that the SOD and, above all, ME impact categories show the least reduction in environmental damage, both in the case of stems and leaves valorization.

Finally, in the case of UAE, a 25% reduction in electricity needs has been studied, given its important environmental contribution to the profile of this alternative. The values obtained between the leaf and stems valorization scenario are analogous, with an overall average reduction of 61% and 63%, respectively (**Figure 10**). The highest reduction value is reached, in both cases, for the FET and MET categories, around 90%, while the categories with the lowest improvement value are ME, with an average of 36% between stems and leaves, SOD, with 38% and FRS, with 37.5%.

12.8 Eco-efficiency analysis

In order to evaluate both environmental and economic assessment in a single score value, which encompasses both, an eco-efficiency analysis is developed. The development of the eco-efficiency assessment is considered a comprehensive and systematic approach to identify the most suitable biorefinery scenarios under a sustainable perspective. It is a useful tool to be applied by companies and policy makers aiming at achieving more sustainable production schemes, while preserving the economic viability of a production scheme. For this reason, it has been considered to include this analysis for the extraction scenarios presented, as the scores obtained are useful for selecting the best extraction alternative, given the quantification of both environmental and economic burdens. To this end, three eco-efficiency perspectives have been evaluated, the first of which takes into account the relationship between the minimum selling price of the antioxidant and the environmental burden, the second the operating costs and environmental impacts, and the third the relationship between production capacity (kg of antioxidant produced annually) and, again, environmental loads.

For the first eco-efficiency scenario (**Figure 11**) nearly all the extraction alternatives are embedded in the green region, that is representative of an eco-efficient scenario. An exception of four scenarios is observed, being M_L, SFE_L and S_S the ones categorized in the intermediate region between being eco-efficient and being non-eco-efficient, for the impact

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categories of GW, FE and TET, while for the FE, the SFE_L goes for the eco-efficient region, while UAE_L and SFE_S move from the eco-efficient region to the intermediate zone. On the other hand, the M_S scenario is non-eco-efficient for all the impact categories under evaluation, as it is in the red region. In order to enhance the ratios observed, in the case of the M_L scenario, the improvement should be based on increasing the production capacity or reducing the associated production costs to lower the minimum selling price of the antioxidant produced. While for the case of the SFE_L, S_S, UAE_L and SFE_S the trend may be focused on reducing the associated environmental burdens, since the minimum sales prices are in line with the other extraction alternatives. Given these first results, it could be considered that the extraction alternatives of UAE_S, PLE_S, PLE_L, S_L are the most promising in terms of the ratio between the minimum selling price and the associated environmental burden.

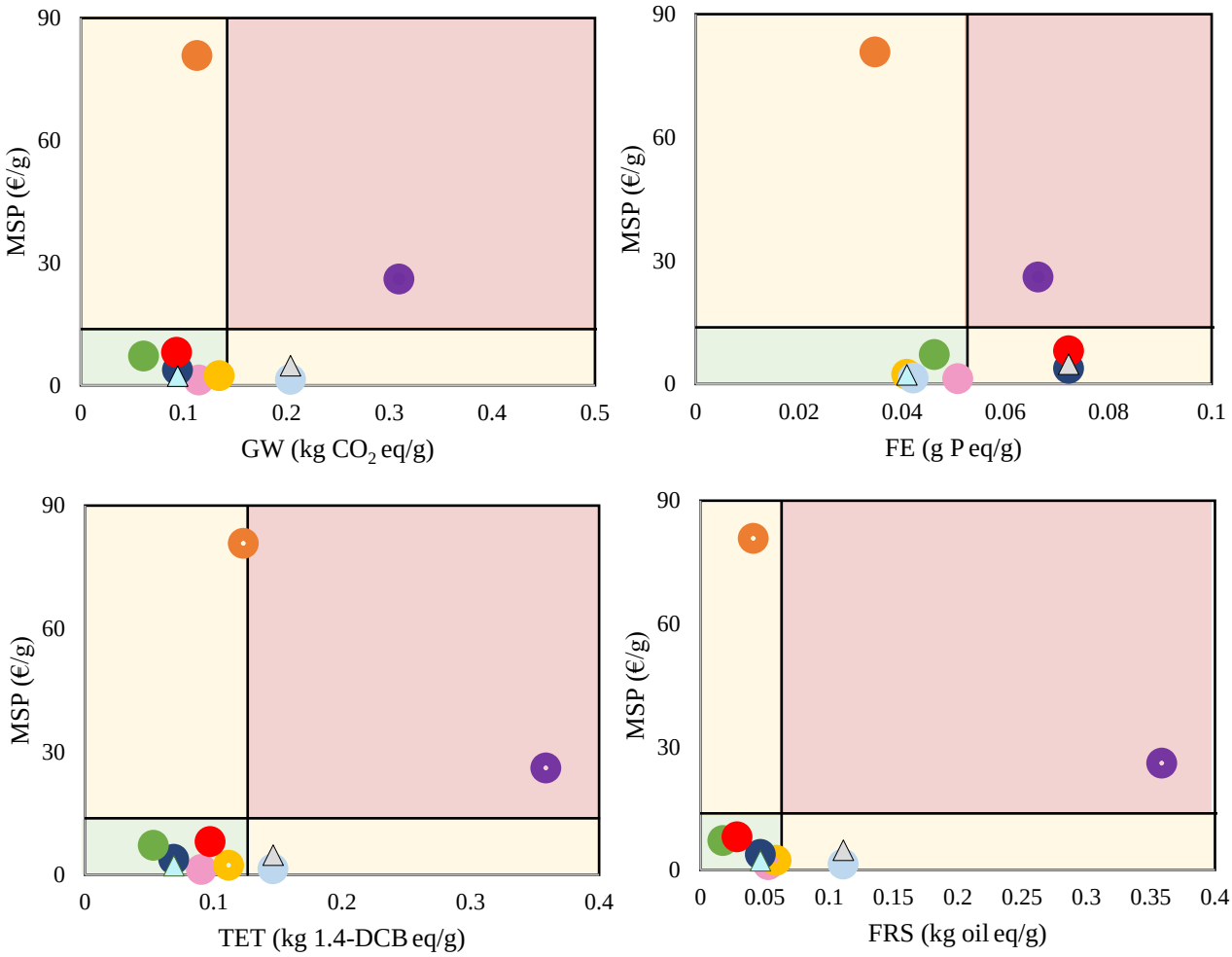

Figure 11. Eco-efficiency analysis considering the index between the minimum selling price (MSP) and the environmental loads. Color code: ●M_S, ● M_L, ● PLE_S, ● PLE_L, ● SFE_S, ● SFE_L ● UAE_S, ● UAE_L, △S_S and △S_L.

When evaluating the score related to the ration between operating costs and environmental loads, significant variations are obtained in comparison to the previous eco-efficient analysis. The M_S extraction alternative is no longer a non-eco-efficient scenario, as it is now located in the intermediate region for all the impact categories evaluated, taking into account that the main

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problem of not being eco-efficient are the related environmental loads, rather than the operating costs, which are below the average value of all the scenarios. In this case, the non-eco-efficient scenarios are those of SFE_L and S_s for the GW, TET and FRS impact categories, while the SFE_S. UAE_L and S_S for the FE one. The rationale behind these scores weighs more heavily on operating costs than on the associated environmental costs, with the exception of the FE impact category, where both items are higher than the average for the scenarios.

Moving to the intermediate region, the yellow ones, in the GW, TET and FRS impact categories, the scenarios of S_L, SFE_S, PLE_L and M_S are the ones categorized under these regions. For the three first extraction alternatives, improvement actions should be based on the reduction of the operating costs, as they are significantly higher than average, while in the case of the M_S scenario, the main objective should be the reduction of the related environmental burdens, as they are substantially higher compared to the other scenarios.

Therefore, given the scores obtained after the evaluation of the second eco-efficient alternative, it can be concluded that the most suitable extraction scenarios, i.e., those in the green region for all the impact categories evaluated, are PLE_S and M_L, being the UAE_S and UAE_L right on the dividing line or frontier between the eco-efficient and intermediate region.

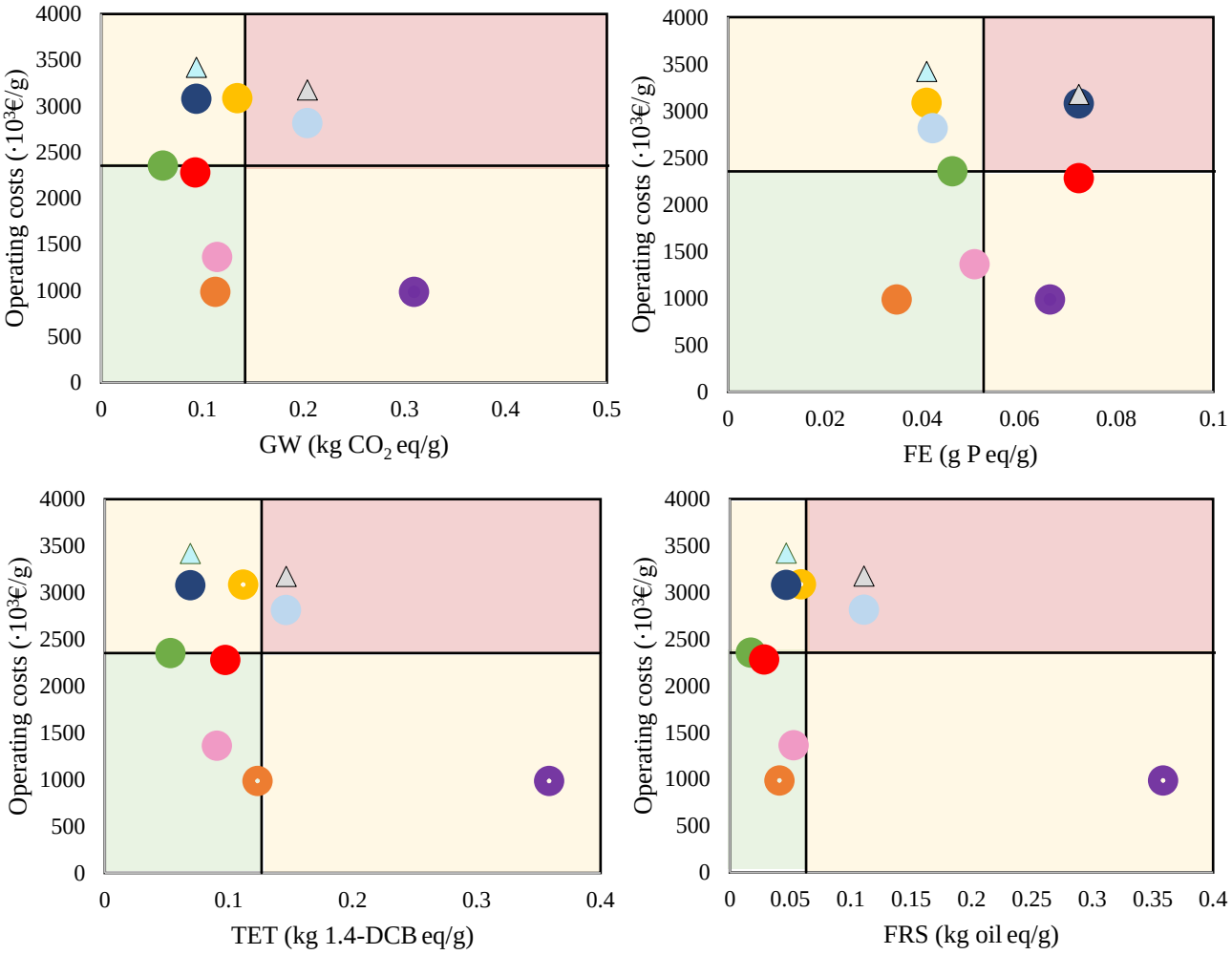

Figure 12. Eco-efficiency analysis considering the index between the operating costs and the environmental loads. Color code: ●M_S, ● M_L, ● PLE_S, ● PLE_L, ● SFE_S, ● SFE_L ● UAE_S, ● UAE_L, △S_S and △S_L.

The production capacity of a waste stream valorization scenario is one of the most important aspects in assessing the ability to generate economic benefits and thus to demonstrate the economic viability of a large-scale process alternative (**Figure 13**). Therefore, in this third eco-efficiency scenario, the ratio between the capacity to produce antioxidant and the associated environmental impacts is studied. A greater number of differences are observed between the impact categories evaluated, although it can be observed that three extraction strategies are always found in the eco-efficiency region, these being PLE_L, PLE_S and S_L.

On the contrary, there are two alternatives that have been in the non-eco-efficient region, that of S_S and that of M_S, a similar result to the eco-efficiency cases evaluated above. The main reason for their categorization in this region of the figure is the associated high impact, in the case of the S_S scenario and the low productive performance for the M_S scenario.

On the other hand, considering the scenarios located in intermediate regions, it can be observed that, in the case of the SFE_L alternative, the main problem is the associated impact, greater than average, except in the FE category, where it is positioned in the eco-efficient region. Regarding the alternatives of UAE_S and M_L, they are in the intermediate region for all the impact categories evaluated, given their low antioxidant production capacity. In the particular case of the extraction alternative UAE_L, it is observed that for the impact category FE it goes from being in a situation of intermediate eco-efficiency to one of no eco-efficiency. Given the results obtained, the alternatives that are encountered on the eco-efficient region are the ones of PLE_L, PLE_S and S_L.

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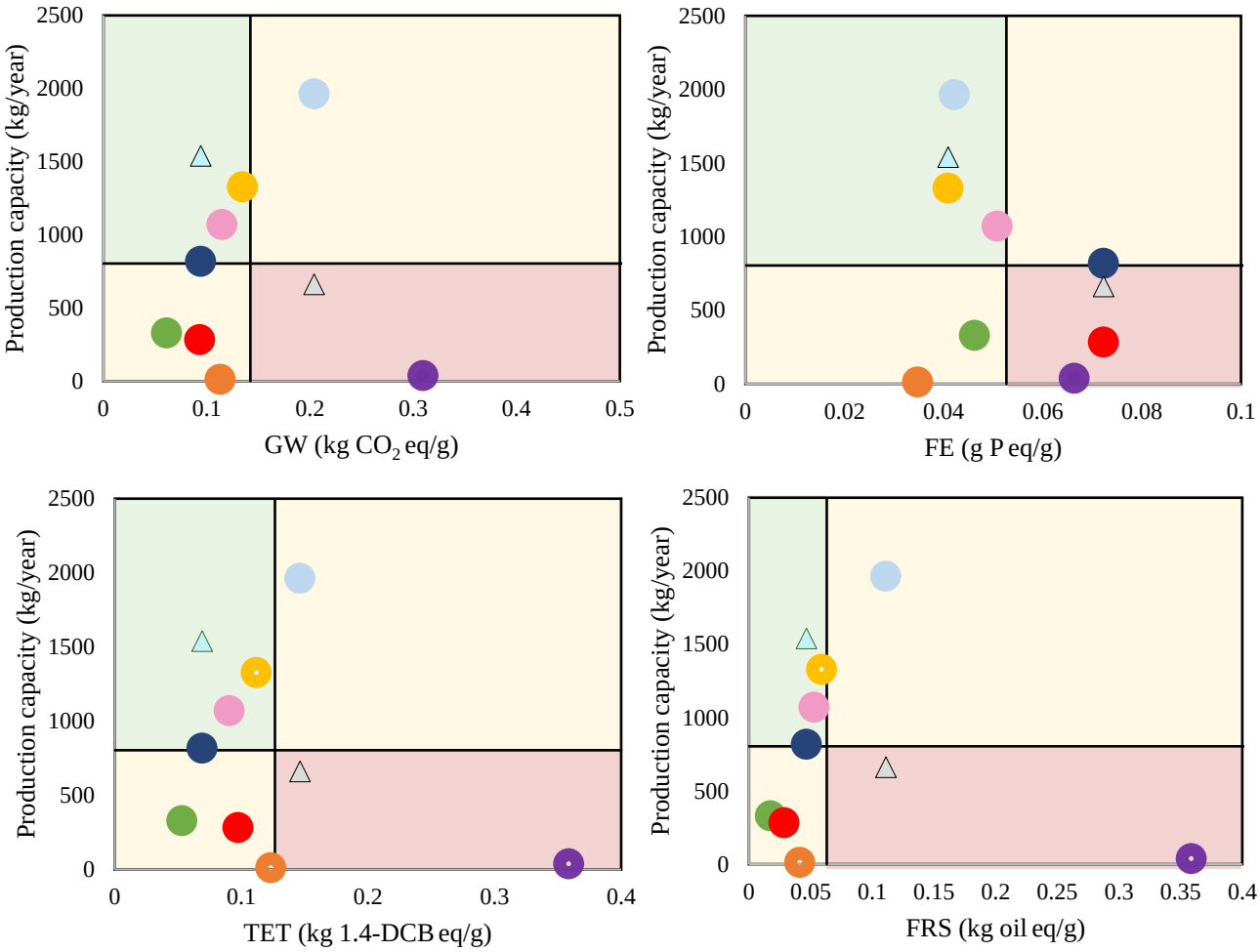

Figure 13. Eco-efficiency analysis considering the index between the production capacity and the environmental loads. Color code: M_S, M_L, PLE_S, PLE_L, SFE_S, SFE_L UAE_S, UAE_L, △S_S and △S_L.

Given that different eco-efficient values are obtained, as well as given the huge number of scenarios under evaluation, per extraction alternative, to select the best option under both an environmental and economic approach, **Table 17** includes an overall evaluation of the index obtained per category and per extraction procedure. In order to have a "quantitative value" it has been thought to apply numerical score according to the classification of the scenario: for the eco-efficient region, a value of 10 is given, for the intermediate one, a score of 5, and the non-eco-efficient has an index of 1. Given these assumptions, the scenario that achieves an eco-efficient categorization for all the evaluated indices achieves a final score of 30 (10 for the index 1 (MSP versus environmental loads), 10 points for the index 2 (operating costs vs environmental loads) and 10 points for the index 3 (production capacity against environmental impacts).

Once the quantification methodology used for the comparison has been described and implemented, it is noted that the extraction alternative of PLE using the leaves from beet waste is the most suitable, since all its indices are embedded in the eco-efficiency region, thus reaching the maximum value of 30 points (**Table 17**). While the recovery of stems, using this same extraction strategy, is also promising, since it reaches both index 1 and 3 full eco-efficiency

values, while for index 2 it is in an intermediate position, where it has been detected that the reduction of operating costs is the key to make it a fully eco-efficient option.

Promising values are also obtained for the UAE and Soxhlet extraction methods, for the stems and leaves valorization, respectively. For the UAE_L alternative, in both indexes 1 and 2, full eco-efficient is achieved, while for the index 3, the production capacity should be increased to be categorized as eco-efficient, while for S_L, the problem is found in index 2, given the associated production costs that are related to the production scheme, which needs to be significantly reduced (**Table 17**).

As for the scenarios with the lowest scores, two are the most outstanding, maceration and Soxhlet, as they only reach a final score of 7/30, with the maceration and Soxhlet strategies for stem valorization being the referent ones (**Table 17**). Regarding the M_S scenario, both indices 1 and 3 are categorized in the non-eco-efficient region, while for index 2, advocating the reduction of environmental loads is the main strategy to try to improve its potential eco-efficiency. In the case of the S_S scenario, the intermediate region is reached for index 1, being once again the high related environmental impacts the main reason behind the inefficiency of the process, being therefore this item where more efforts should be put for its improvement.

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Table 17. Comparison between the eco-efficient scores obtained for the alternative extraction scenarios. Acronyms: EI (Environmental Impact), P (Production capacity). Number in brackets represents the number of categories of impact that achieved that categorization.

Index	**€/ impact**			**€/ impact**			**kg products / impact**			**Global assessment**	
Scenarios	Minimum selling prince/EI			Production costs/EI			Production capacity/EI			Score	*Preference*
	Eco	*Middle*	*Non-Eco*	*Eco*	*Middle*	*Non-Eco*	*Eco*	*Middle*	*Non-Eco*		
● M_S			✘ (4)		↓EI (4)				✘ (4)	7.00	**7th**
● M_L		↓€ (4)		✓ (4)				↑P (4)		20.00	**4th**
● PLE_L	✓ (4)			✓ (4)			✓ (4)			30.00	**1st**
● PLE_S	✓ (4)				↓€ (4)		✓ (4)			25.00	**2nd**
● SFE_L	✓ (3)	↓EI (1)			↓EI (3)	✘ (1)		↓EI↑P (4)		17.75	**5th**
● SFE_S		↓EI (4)			↓€ (1)	✘ (3)	✓ (1)	↓EI (3)		13.25	**6th**
● UAE_L	✓ (4)			✓ (4)				↑P (4)		25.00	**2nd**
● UAE_S	✓ (3)	↓EI (1)		✓ (3)	↓EI (1)			↓EI↑P (3)	✘ (1)	22.50	**3rd**
△ S_S		↓EI (4)				✘ (4)			✘ (4)	7.00	**7th**
△ S_L	✓ (4)				↓€ (4)		✓ (4)			25.00	**2nd**

12.9 Main conclusions achieved.

Chapter 12 has been based on the evaluation and assessment of different extraction technologies for the valorization of beet wastes as resources for the extraction of antioxidants. Both beet leaves and stems have been considered as process inputs, with the use of five extraction technologies. To develop the environmental and economic assessments, a large-scale simulation of the scenarios has been performed from laboratory-scale literature data, using the SuperPro Designer tool, and considering a production capacity of 100 kg/batch of beet residues.

The environmental profiles and impact values obtained have revealed that the best extraction techniques are SFE and PLE, as they have the lowest environmental load. In the case of UAE, significant improvements are necessary, as very high environmental values are obtained, mainly due to the high electrical demand required for the extraction process. On the other hand, the LCA results have indicated that the main hot spot was the electricity demand, followed by steam requirements and solvent production. Regarding the economic evaluation, it has been found that opting for the emerging technologies of SFE and PLE offers a wider economic feasibility, together with the maceration one, as the minimum selling prices of the resveratrol obtained is slightly lower in comparison to the UAE alternative but significantly reduced when compared to the Soxhlet one.

Given the results obtained, in order to provide a final score of the technologies evaluated, an eco-efficient analysis encompassing both environmental, economic and modelling results was also developed. The scores obtained showed that the most promising extraction technology is PLE, which is in line with the previous results obtained. On the other hand, it is important to mention as a final conclusion that the evaluation of antioxidant recovery from beet wastes using these economic and environmental approaches confirm the potentiality of these waste streams as valuable resources for the extraction of antioxidant compounds and the validity of green technologies as extraction techniques to replace conventional ones.

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13

Valorization of food and forestry related side streams to produce resveratrol

This chapter partially reproduces content already submitted, but not published, as "Arias, A., Costa, C.E., Feijoo, G., Moreira, M. T., Domingues, L. (2023). *Environmental and techno-economic assessment on the valorization of vine-side streams to produce resveratrol*. *Submitted to Science of the Total Environment journal*." and "Arias, A., Costa, C.E., Feijoo, G., Moreira, M. T., Domingues, L. (2023). *Process modeling, environmental and economic sustainability of the valorization of whey and eucalyptus residues for resveratrol biosynthesis*. *Submitted to Waste Management journal*.".

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SUMMARY

One of the most promising alternatives to cope with the environmental deterioration and the management of waste generated daily is the development of biotechnological processes based on the valorization of these waste streams according to their content in compounds of interest. In this context, the regions of Galicia and Portugal have large areas of land dedicated to forestry, agricultural and livestock, generating a large amount of waste, whose management, far from producing a benefit, represents a cost for the producer. The importance of these facts has awakened a great interest in society to focus their interest in improving the current situation while seeking a benefit, both environmental and economic, of the existing resources. That is why the integration of biotechnological and biorefinery processes for their valorization are considered as key aspects in the way of trying to give a second life to these wastes, towards the production of high added value bioproducts.

Waste streams related to wine and cheese production, and those residues from forestry activities, could be valorized through a biotechnological approach to produce resveratrol, an antioxidant compound with wide application on different sectors, as pharmaceutical, food and cosmetics, among others. Process modeling at real production scale, considering a production capacity of 100 ton/batch of residual input is developed using the SuperPro Designer software, based on laboratory results on resveratrol production, with the objective of analyzing the mass and energy balances related to the process. In addition to this modeling, the economic analysis is also developed, as it provides valuable information on the possible commercialization of resveratrol obtained through this valorization route. Furthermore, by applying the Life Cycle Assessment methodology, it is possible to identify the environmental burdens and the profile of the scenarios under evaluation, seeking to estimate the damage potential.

Chapter 13 proposes a biotechnological process to produce resveratrol from wine residues (vine pruning, grape must and wine lees), whey from the dairy industry and eucalyptus residues from forestry exploitation, given the huge amount of those residual streams produced yearly. In order to evaluate its suitability, a techno-economic analysis and an environmental assessment have been carried out using the Life Cycle Assessment (LCA) methodology, together with a modelling of the alternatives by using the SuperPro Designer tool.

The results are used to verify and discuss the potential of these valorization scenarios both from an economic point of view, by obtaining a minimum selling price of resveratrol that ensures the viability of the process below the market average, and from an environmental point of view, using the ReCiPe methodology to evaluate the environmental loads and associated profiles. In addition to the aforementioned reports, **Chapter 13** also includes sensitivity analysis and eco-efficiency assessment in order to integrate economic, environmental and productivity scores into a single image, thus providing an cohesive view of the scenarios under a sustainable approach.

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13.1 Food and forestry side-streams as biorefinery feedstocks

The European Union is the leading producer and exporter of wine, with Italy, France, Portugal and Spain leading the ranking of countries with the highest annual global production shares (Zacharof, 2017). The annual production of 75 million tons of wine grapes involves large volumes of secondary streams, as well as on-site emissions, wastewater, solid waste and biosolids (Bucić-Kojić et al., 2022; Ioannidou et al., 2022).

Wine production is divided into four main stages, starting with destemming and crushing of harvested grapes to remove stems, so that crushed grapes and must are obtained before the alcoholic fermentation stage. Once fermentation is complete, the pressing phase removes skins and seeds, so that the broth is sent to an aging and stabilization stage. This part of the process is the most time-dependent and is where the remains of yeast and grape solids settle at the bottom of the equipment and are removed, known "wine lees" residues (Cañón et al., 2014; Ncube et al., 2021; Rodrigues et al., 2022).

The secondary streams from the winemaking process could be considered as a potential biomass resource amenable to a biorefinery scheme given their composition in lignocellulosic compounds, fermentable sugars and antioxidants (Filippi et al., 2022; Gonzalez-Garcia et al., 2018; Kucharska et al., 2018). Vine pruning (VP) residues are the most significant by-product of viticulture, representing more than 90% by mass. Its management as burning in the agricultural field or its use as compost can be changed according to circular economy strategies. Its composition and availability, together with its low cost make this residue a potential feedstock as source of fermentable sugars after a pretreatment stage (Jesus et al., 2022; Wei et al., 2022). In this sense, it has been reported that two main valorization alternatives could be developed: (1) separation and extraction of high-added value compounds, such as flavorings, pigments or phenols (Jesus et al., 2020) and (2) bioconversion strategies, in which fermentation procedures stand out, for the production of biochemicals, biofuels, enzymes and/or antioxidants, among others (Berbel and Posadillo, 2018; Jesus et al., 2017; Kalli et al., 2018; Winterhalter et al., 2015; Zacharof, 2017). In the particular case of low-quality wine, it is possible to produce a number of value-added products such as antioxidants, nutrients, ethanol, microbial oil or even bioplastics (Hijosa-Valsero et al., 2021; Kopsahelis et al., 2018; Maina et al., 2017).

Regarding cheese whey (CW), the annual production of this side stream in the world amounts to 21,600 thousand tons, as 9 L of whey are obtained per kg of cheese produced. This stream presents a characteristic high concentration of lactose, which implies a high organic load: around 1200-1800 mg/L BDO_5 (Arias et al., 2021; Carvalho et al., 2021; Lappa et al., 2019; Lopes et al., 2019a). Its content of biological oxygen demand (BOD), around 1200-1800 mg/L, could result in important impacts on the aquatic ecosystems (Bendicho and Lavilla, 2019; Sirmacekic et al., 2022). The oxidation of the organic matter will reduce the oxygen available to aquatic organisms, resulting in their death. In this sense, it could be thought that environmental impacts related to eutrophication will be the most affected by the non-management of this side-stream (Cruz-Salomón et al., 2020; Zandona et al., 2021). In fact, it has been reported that the mismanagement of cheese whey could involve a polluting capacity more than 100 times higher than that caused by domestic wastewater (Lopes et al., 2019b).

The first and simplest approach for the management of this stream is the recovery of its protein content (around 7 g/L), consists of its fractionation through a series of ultrafiltration units, thus obtaining a high-protein stream, which may reach a wide range of end-users (Buchanan et al., 2023; Yadav et al., 2014). However, as the lactose content is much higher (around 45 g/L), additional valorization alternatives to protein recovery can be proposed, such

as the approach of its management as a source of fermentable sugars for the microbial production of high value-added compounds such as bioactive materials, bioplastics, biofuels and/or enzymes, among others (Buchanan et al., 2023; Guimarães et al., 2010; Nayak and Pal, 2013; Zhou et al., 2019).

With respect to eucalyptus residues (ER), about 46% of the total forest biomass is managed as residues, representing 37.7 m^3 per hectare (Edzik et al., 2022; Tripathi et al., 2019). Its management typically relies on its energy recovery, although its use has been considered for the production of particleboard, which would be produced from 50% virgin material and 50% residual material, meeting the requirements established in the EN 312 standard (Devasahayam et al., 2022; Iwakiri et al., 2017).

However, given the huge amount of wood products produced, new strategies are required to valorize the volume of annual forest residues. Some studies have evaluated these recoveries through biofuel production, although improvements are needed to reduce process costs, especially regarding feedstock pretreatment (Goswami et al., 2023; Karthik et al., 2023; Romaní et al., 2019, 2016, 2014), others have considered fermentation process to produce bioactive compounds (Arias et al., 2023; Gaspar et al., 2019; Tavares et al., 2020) or even their direct disposal in the forest to maintain soil fertility (Pergola et al., 2022).

The rationale for the development of new process strategies for the valorization the aforementioned side streams is related to the significant environmental impacts associated with its management and/or disposal. With this in mind, the valorization of winery side streams produced in companies from the Douro region of Portugal is addressed in this chapter, since it is the region with the largest production of wine annually (Gaspar et al., 2019), as can be seen in **Figure 14**.

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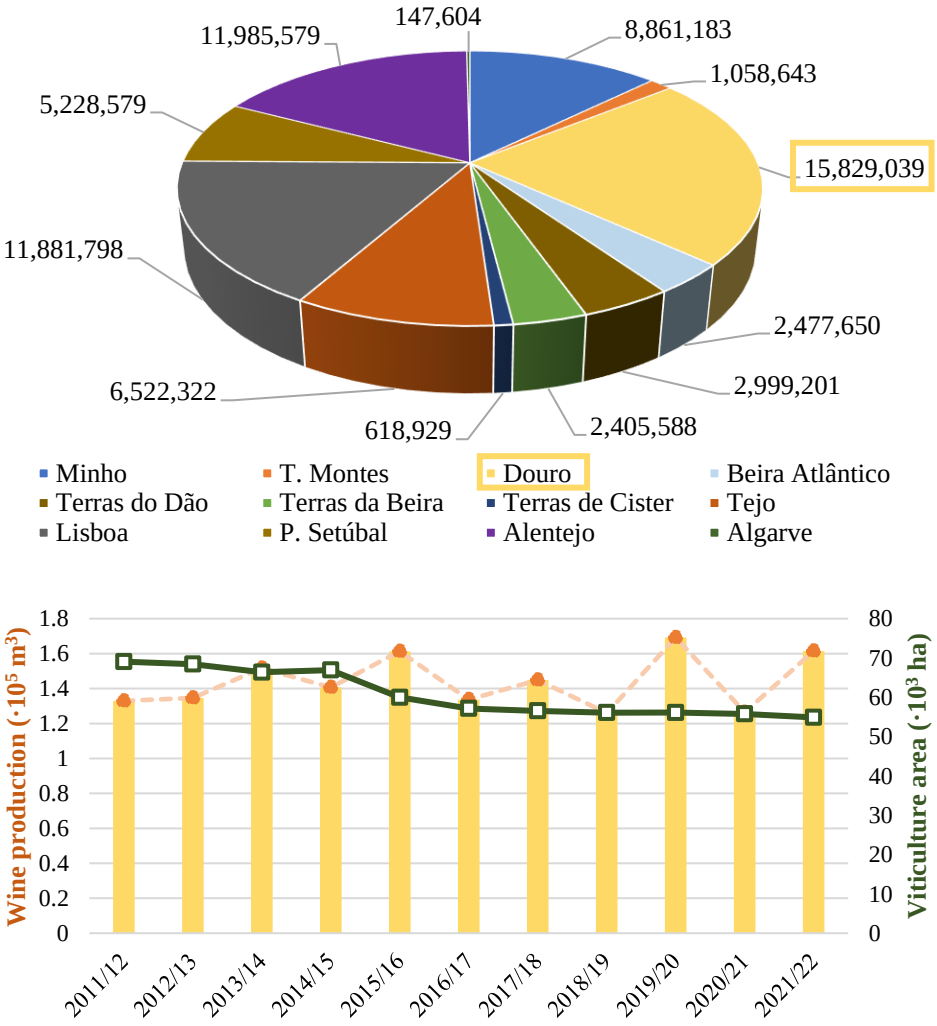

Figure 14. Winery production data. Above figure: total amount of wine produced in EU countries from 2011 to 2022 (in volume base, hL). Below figure: wine production (—●—) and viticulture harvesting area (—□—) of Douro Region. Source: Own elaboration.

According to the IDEPA (Institute for Economic Development of the Principality of Asturias) and to the Spanish Minister of Agriculture, Fishing and Food, $5.48 \cdot 10^5$ ton of cheese has been produced, which has derived on the production of $2.55 \cdot 10^6$ ton of cheese whey, being Spain the 6th higher cheese producer in Europe (Eurostat database). **Figure 15** depicts the evolution on the production of cheese on the Spanish region from 2010 to 2021, according to the European database. As can be seen, since 2014 the amount of cheese produced is higher than the European average, thus demonstrating that Spain has an important contribution in the value chain of the European market for this product.

On the other hand, as for the secondary flows of cheese production, while in the past they were considered only for animal feed, today they have become a high value-added product in the food industry, mainly as a food supplement. The trend of cheese whey valorization is continuously growing, especially due to the growing concern for maintaining active and healthy aging, along with good physical condition (Gamlath et al., 2023; Lavelli and Beccalli, 2022; Mehra et al., 2021).

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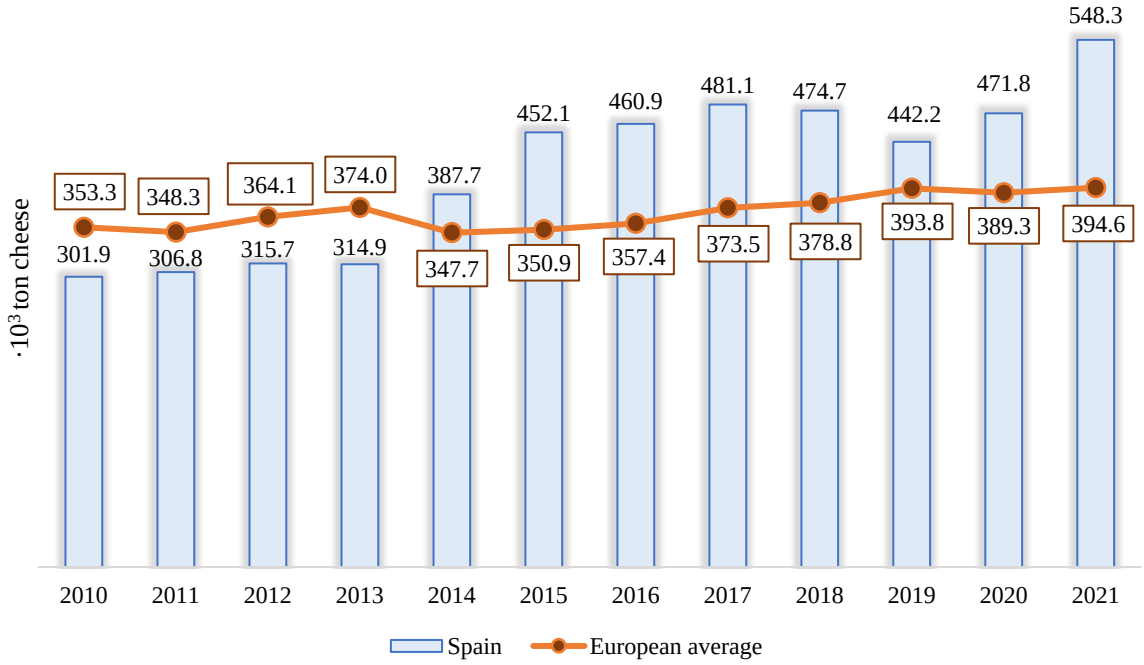

Figure 15. Production of cheese in Spain and its comparison with the European average from 2010 to 2021. Data obtained from the European database. Own elaboration.

Lastly, with respect to eucalyptus residues, it should be mentioned that both Spain and Portugal are one of the most important producers of this wood species, with a total combined are of harvesting that amounts to more than 1.4 million ha (Cerasoli et al., 2016). Given this huge plantation area, while timber harvesting and processing into other wood products is taking place, the amount of wood residues produced is very high (including branches, leaves, bark, chips, etc.). For example, in the United Kingdom 4.5 million tons of wood waste are produced, of which only 1.3 million tons are recycled, while in Italy 63% of the total waste, or 2 million tons, is recovered and reused (Fava et al., 2021; Pandey, 2022). But perhaps the most outstanding figure is that of the United States, where wood waste produced amounts to 18.1 million tons per year, of which only less than 20% is valorized (Nguyen et al., 2023). The main problem is that these wood residues are often exported, burned to produce energy, which implies a considerable level of emissions, or simply managed as waste, without being fully utilized, thus losing their value. This is why the wood sector should focus on their use as a fundamental aspect, since it would mean greater economic efficiency and a greater circularity of the process. **Figure 16**, elaborated using the *Bioreg Geoportal tool*, shows the main wood waste recovery strategies, including energy recovery, mixed strategies and recycling, in order to provide a broad view of wood waste management practices at the European level.

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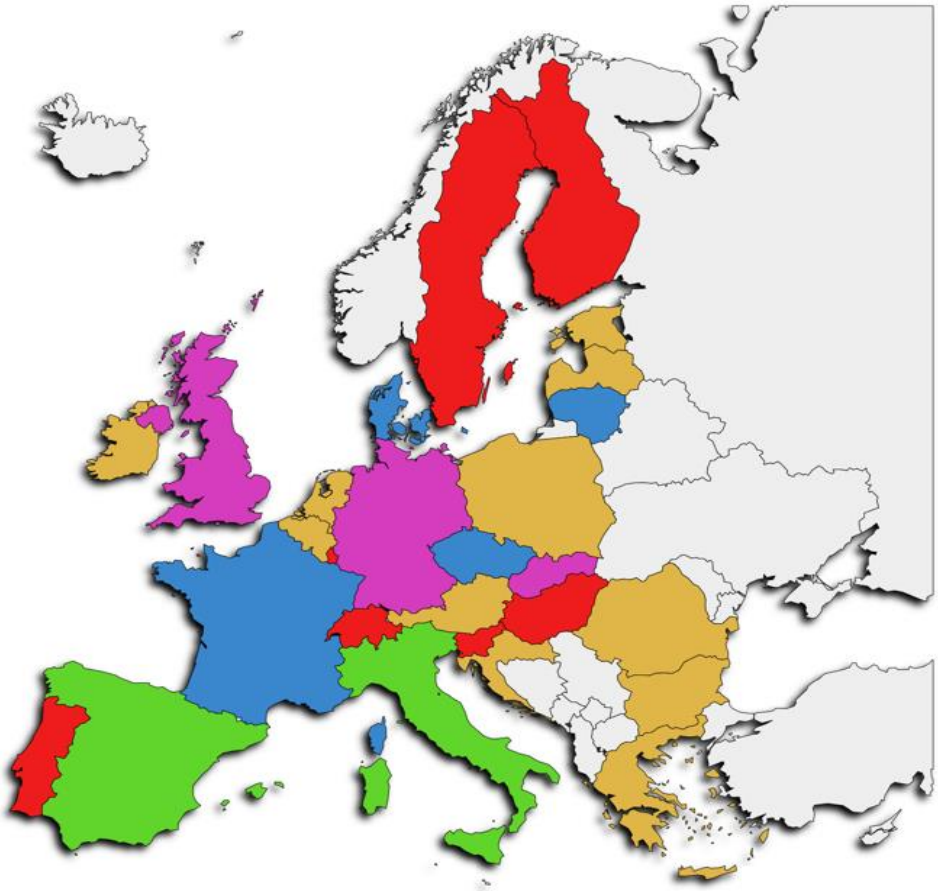

Figure 16. Recovery strategies for wood waste. Colour legend: ■ energetic valorization, ■ mixed strategies but oriented to energy, ■ mixed strategies but oriented to recycling, ■ mixed strategies and ■ recycling. Source: Own elaboration.

For this reason, the aforementioned secondary flows are analyzed from the point of view of the conceptual design of processes, their techno-economic and environmental analysis. To do so, the experimental results obtained for resveratrol production with and genetically modified strain of *Saccharomyces cerevisiae* strain were considered (Costa et al., 2022b, 2022a, 2021). Resveratrol is a polyphenol with two phenolic rings linked together by an ethylene bridge (Gambini et al., 2015; Salehi et al., 2018). Its market value is high, given its interesting properties, as it is antioxidant, anti-inflammatory, anti-aging, neuroprotective and anticarcinogenic, so its presence in the nutraceutical, pharmaceutical and food markets is expected to be high (Jabbar et al., 2022; Piyaratne et al., 2022; Rabesiaka et al., 2011).

Bearing this in mind, it is expected that the process of obtaining resveratrol by the valorization of these flows is economically viable. To verify this, a techno-economic analysis of the large-scale process will be performed by modeling the biotechnological process (Costa et al. 2021, 2022) using the SuperPro Designer software. In addition, a life cycle analysis (LCA) is also developed to obtain the environmental profile, such as the contribution of each of the elements of the process to the environment.

13.2 Process description and scale-up modelling

The production process scheme differs slightly among the food-related and forestry waste streams used as feedstock, as vine pruning (VP) and eucalyptus residues (ER) require a

pretreatment step for the release of fermentable sugars, while for grape must (GM), wine lees (WL) and cheese whey (CW), no pretreatment is required. **Figure 17** depicts the main stages of each of the process scheme scenarios developed for the valorization the aforementioned side-streams, also considering the agricultural and forestry activities, as well as the background process related to harvesting, together with the production process itself. Furthermore, it is worth mentioning that the modeling approach is based on the valorization schemes of the secondary streams, not on the part of the wine or cheese production process, although, for the development of the environmental assessment through the LCA methodology, the background activities, both the viticulture, forestry, cheese and wine production process, are considered. On the other hand, regarding the operating conditions, chemicals needed and process efficiency in the production of resveratrol, the results obtained by the research report developed by Costa et al. (2022) and Baptista et al. (2023) have been considered (Baptista et al., 2023; Costa et al., 2022a).

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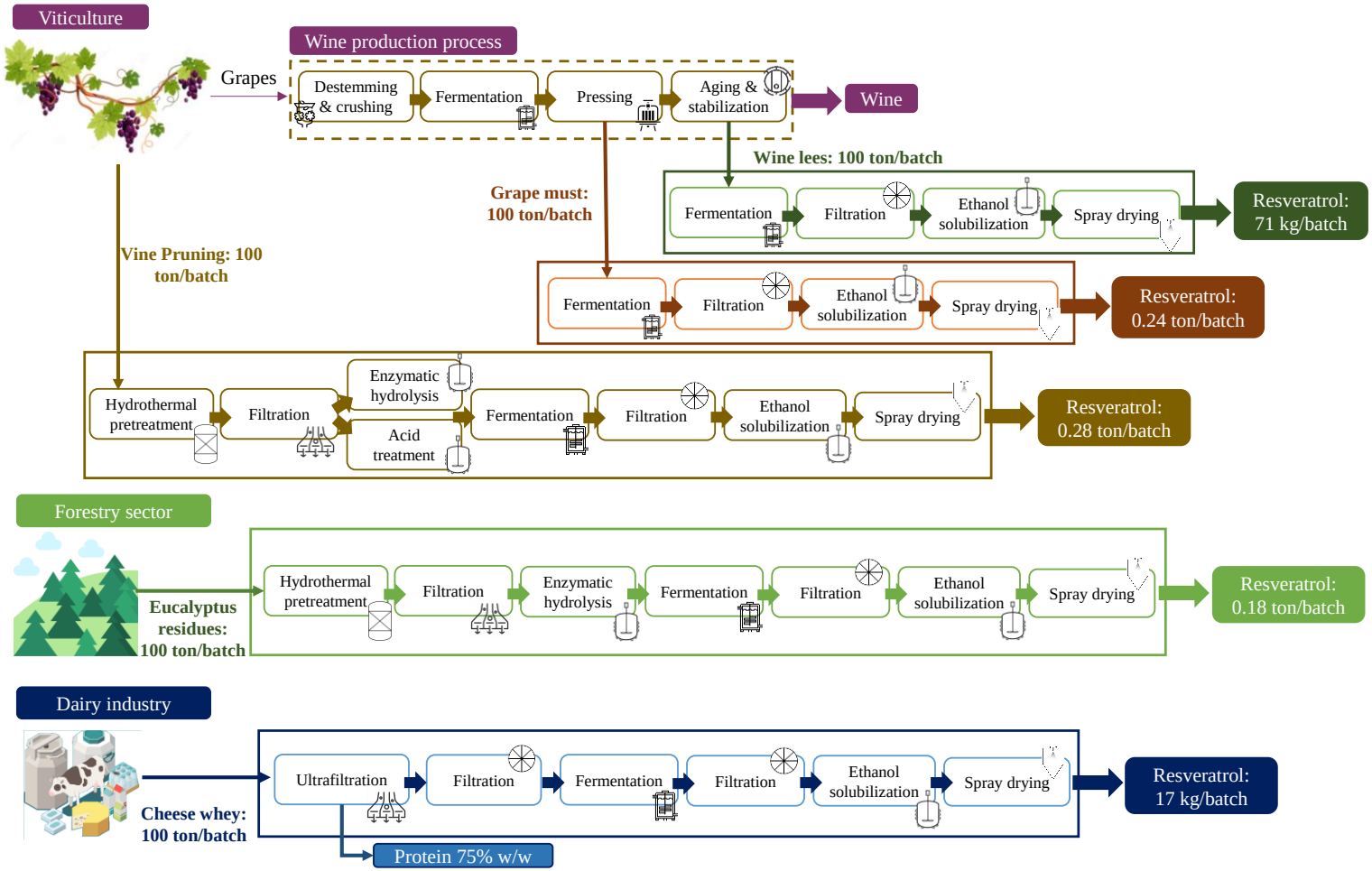

Figure 17. Main stages of the biorefinery approach of wine production, forestry sector and dairy industry side-streams valorization alternatives. Source: Own elaboration.

Table 18 shows a summary of the process parameters and variables considering as input flow 1000 ton/batch of each of the side streams (VP, GM, WL, CW and ER). The characteristic details of each process as a function of the processed stream are presented below. The VP and ER residues require a hydrothermal pretreatment (liquid-to-solid ratio of 8 kg water/kg VP, 215°C, severity of 3.89) carried out in a plug flow reactor (PFR-101, **Figure 1SM** and **Figure 2SM**). Afterwards, a filtration step is required (BF-101**, Figure 1SM** and **Figure 2SM**), in which the solid fraction undergoes an enzymatic hydrolysis treatment (R-101, **Figure 1SM**) (using Cellic CTec 2 as enzyme, 626 U/mL, 24 h and 45ºC) and the liquid fraction undertakes a chemical post-hydrolysis (R-103, **Figure 1SM**) with sulfuric acid (72% w/v at 121ºC), in the case of the VP residues, while for the ER it consisted on a single enzymatic-acidic stage (**Figure 2SM**). These two processes of both the solid and liquid fractions provide a higher release of fermentable sugars, and therefore an increase in the yield of the process.

After the pretreatment stage, which encompasses both liquid and solid fractions, the fermenter of the process (FR-101, **Figure 1SM** and **Figure 2SM**) operates in batch regime with glucose and xylose levels of 40 g/L and 24 g/L respectively and 7.5 g/L of yeast extract as nutrient source, room temperature, constant agitation and 96 h. After the fermentation section, the fermentation broth is sent to a filtration stage (RVF-102, **Figure 1SM** and **Figure 2SM**), to remove the biomass to continue with the purification of resveratrol thanks to its extraction with ethanol (V-103, **Figure 1SM** and **Figure 2SM**). After separation of the remaining components in the product stream (S-134, **Figure 1SM** and **Figure 2SM**), the resveratrol stream is sent to a spray drying stage (SDR-101, **Figure 1SM** and **Figure 2SM**) to obtain resveratrol with 95% purity.

For the case of GM (**Figure 3SM**) and WL (**Figure 4SM**), an analogous process scheme is proposed, except for the pretreatment step, the composition of the fermentation medium and the yield in resveratrol production. In the case of GM, its composition in glucose and fructose amounts to 111 g/L and 116 g/L, respectively, used directly in the fermenter, with the addition of 7.5 g/L of yeast extract, while in the case of WL, the source used to produce resveratrol is the ethanol content, which amounts to 99.3 g/L. The *de novo* biosynthesis of resveratrol from glucose/fructose is accomplished through phenylalanine via the shikimate pathway. Ethanol can also serve as a carbon source and converted into acetaldehyde.

Lastly, with respect to the CW valorization (**Figure 5SM**), an analogous process scheme is proposed, considering a fermentation time of 57 h and a lactose concentration in the fermentation medium of 100 g/L, with a difference in the pretreatment stage. In this case, the cheese whey is partially deproteinized in an incubation stage at 90ºC for 15 min (V-101, **Figure 5SM**). This is an important pretreatment steam of CW valorization as a source of fermentable sugars since the protein content in the fermentation medium could imply a significant decrease in resveratrol production yield. In addition, the use of a centrifuge can accomplish protein separation (DC-101, **Figure 5SM)** to perform the subsequent fermentation, for which a previous pasteurization stage (PZ-101, **Figure 5SM**) is needed. This pasteurization is carried out at 60 ºC in a process time of 1 h.

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Table 18. Production capacity of the different scenarios assessed.

Process	VP	GM	WL	ER	CW
Batch time (h)	327.53	245.25	254.25	99.25	60.25
Number of batches per year	24	31	31	79	131
Batch size (kg resveratrol)	284.40	242.33	71.09	183.19	16.87
Resveratrol production (kg/year)	6,825.6	7,493.57	2,198.32	14,163.85	2,210.50

13.3 Environmental assessment following the LCA methodology

The main objective is the development of the environmental profile of the valorization process of the waste streams from the food and forestry sectors. As for the system boundaries, a "cradle to gate" approach has been chosen, which takes into account all the stages between the extraction of raw materials and the production of resveratrol (Arias et al., 2020). The reason for choosing these boundaries is that, in this case, the focus of the LCA is on assessing the degree of adequacy of the biorefinery process for the identification of the potential of the circular economy model. Furthermore, opening the boundaries of the system towards the consumption of the product by the consumer would imply a broader level of process data, which, at this stage of development, is not available and does not imply a better understanding of the process. To collect the data to build the life cycle inventories (LCI) of the process, the modeling phase, based on the development of mass and energy balances, is used. On the other hand, the functional unit is 1 kg of resveratrol, in line with the objective of the environmental assessment.

Regarding the selection of the calculation methodology, two methodologies have been considered: ReCiPe MidPoint (Huijbregts et al., 2017), consisting of 18 impact categories of which 13 have been selected as the most relevant for the environmental analysis of the valorization of wine side-streams, and ReCiPe EndPoint, through which 3 damage categories are integrated into a single score (**Table 19**). This last calculation methodology provides an overall impact value, which is considered an adequate model for the comparison between the three production schemes, as it simplifies the analysis of the environmental impacts. The identification of the main critical points of the environmental profile will be subsequently used for the fulfillment of sensitivity scenarios aimed at achieving a reduction of environmental loads. In addition, an eco-efficient evaluation is also included, considering as key aspects: minimum selling price, production costs and resveratrol production capacity.

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Table 19. ReCiPe MidPoint and EndPoint categories used for the characterization of the environmental profiles of the wine side-streams valorization scenarios.

Impact category	Acronym	Unit	Impact category	Acronym	Unit
ReCiPe MidPoint methodology					
Global Warming	GW	kg CO_2 eq	Marine Ecotoxicity	MET	kg 1.4-DCB
Stratospheric Ozone Depletion	SOD	kg CFC_{11} eq	Human Carcinogenic Toxicity	HCT	kg 1.4-DCB
Terrestrial Acidification	TA	kg SO_2 eq	Human Non-Carcinogenic Toxicity	HNCT	kg 1.4-DCB
Freshwater Eutrophication	FE	kg P eq	Land Use	LU	m^2a crop eq
Marine Eutrophication	ME	kg N eq	Mineral Resource Scarcity	MRS	kg Cu eq
Terrestrial Ecotoxicity	TET	kg 1.4-DCB	Fossil Resource Scarcity	FRS	kg oil eq
Freshwater Ecotoxicity	FET	kg 1.4-DCB			
ReCiPe EndPoint methodology					
Human Health	HH	Pt	Ecosystems	ES	Pt
Resources	RS	Pt			

13.4 Techno-economic analysis

Seeking to identify the economic feasibility of the proposed scenarios, an economic evaluation was developed considering the costs of equipment acquisition, labor, utilities and materials, to obtain the values of the total direct and indirect costs of the plan, the annual operating expenses and the expected revenues obtained from the sale of resveratrol, the target product. In addition, in order to evaluate and compare the three scenarios evaluated, the minimum selling price of resveratrol was calculated, since the yields of the scenarios are different, resulting in a significant variation in the minimum selling price of resveratrol that guarantees the economic viability of the process scheme.

Regarding the calculation of the equipment purchase costs, the equations and tables available in literature (Smith, 2005; Towler and Sinnott, 2021) have been considered in order to provide as accurate a value as possible of the purchase costs, since these equations take into account the data obtained from the process modeling. In this regard, **Equation 1** is used to calculate the purchase cost of the equipment according to the Smith methodology, while **Equation 2** is the one related with the Towler and Sinnot recommendations:

$$C_E = C_B \cdot (\frac{Q}{Q_B})^M$$ **Equation 1**

Where CE is the cost of an equipment with a known Q-capacity (\$),
CB is the base cost of an equipment with a known QB capacity (\$), M is a constant that depends on the type of equipment.

$$C_E = (a + b \cdot S^M)$$ **Equation 2**

Where CE is the cost of an equipment with capacity S (\$), a and b are two constants that vary depending on the type of equipment, n is an exponent that depends on the type of equipment.

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Once these equations have been applied, it must be considered that the purchase cost obtained must be updated to 2023. For this purpose, the CEPCI (Chemical Engineering Plant Cost Index) indexes have been taken into account and **Equation 3** has been applied.

$$\frac{C_{E1}}{C_{E2}} = \frac{Index\ 1}{Index\ 2} \qquad \textbf{Equation 3}$$

Where CE_1 refers to the equipment purchase cost in year 1 ($), CE_2 to the equipment cost in year 2 ($), Index 1 to the CEPCI index in year 1 and Index 2 to the CEPCI index in year 2 (2023). To this end, when the Smith equation is used, the values of the parameters are based on the year 2000 estimates, whose CEPCI index is 394.1, and when the Sinnot equation is used, the parameters are estimated for the year 2006 with a CEPCI index of 478.6.

For the development of the techno-economic evaluation, other assumptions and considerations have been made: a construction period of 30 months and 4 months for start-up, a useful life of the project of 30 years, an inflation of 4% and an income tax of 25%. As for the operating capacity of the plan, it operates at 100% of its production capacity for 11 months per year, using 1 month for periodic maintenance of the facilities.

13.5 Results

13.5.1 Process modelling

The design of the equipment (i.e., volume, drying capacity, filtration speed, etc.), as well as the number of equipment required to treat a total of 100 ton/batch of feedstock, either VP, GM or WL wine side-streams, was conducted. In this regard, the main equipment, their required number and characteristics are depicted in **Table 20**, for the case of using VP as substrate, **Table 21**, when using GP as feedstock, **Table 22** for WL as resource, **Table 23** for the case of using ER and **Table 24** when CW is used for resveratrol production. As previously mentioned, the VP and ER side streams require a more complex pretreatment than in the case of CW, GP or WL, outstanding that in the case of the pretreatment for the cheese whey is developed with the aim of co-producing WPC that could be sold, thus increasing the functionality and potentiality of the proposed biotechnological procedure. But indeed, this required pretreatment for the ER and VP implies a certain benefit when comparing the alternative production schemes proposed, as those are the feedstock with which a higher amount of resveratrol is produced per batch process, as shown in **Table 18**.

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Table 20. Equipment characteristics evaluation of the biotechnological production process of resveratrol using VP as substrate.

Equipment	Number of units	Label	Equipment characteristic	
Plug flow reactor	1	PFR-101	Volume	2.04 m^3
Flash	2	V-102	Volume	54.82 m^3
Heat exchanger	4	HX-102	Area	88.04 m^2
Belt filter	5	BF-101	Filter capacity	4.5 m^3/h
Stirred reactor	1	R-101	Volume	32.01 m^3
Heat exchanger	2	HX-103	Area	60.44 m^2
Stirred reactor	1	R-103	Volume	390.64 m^3
Rotatory vacuum filter	2	RVF-101	Filter area	167.57 m^2
Heat sterilizer	1	ST-103	Input flux	95.94 m^3/h
Seed fermenter	1	SFR-103	Volume	281 L
Seed fermenter	1	SFR-104	Volume	1.59 m^3
Seed fermenter	1	SFR-105	Volume	7.09 m^3
Heat sterilizer	1	ST-101	Input flux	22.67 m^3/h
Fermenter	2	FR-101	Volume	291.25 m^3
Rotatory vacuum filter	9	RVF-102	Filter area	180.15 m^2
Storage tank	2	V-103	Volume	211.65 m^3
Rotatory vacuum filter	7	RVF-103	Filter area	188.40 m^2
Spray dryer	1	SDR-101	Drying capacity	72.27 kg/s

Table 21. Equipment characteristics evaluation of the biotechnological production process of resveratrol using GM as substrate.

Equipment	Number of units	Label	Equipment characteristic	
Heat sterilizer	4	ST-103	Input flux	83.45 m^3/h
Seed fermenter	1	SFR-103	Volume	1.33 m^3
Seed fermenter	1	SFR-104	Volume	20.92 m^3
Seed fermenter	1	SFR-105	Volume	35.32 m^3
Heat sterilizer	1	ST-101	Input flux	84.77 m^3/h
Fermenter	1	FR-101	Volume	213.17 m^3
Rotatory vacuum filter	4	RVF-102	Filter area	170.11 m^2
Storage tank	1	V-103	Volume	6.95 m^3
Rotatory vacuum filter	1	RVF-103	Filter area	23.38 m^2
Spray dryer	1	SDR-101	Drying capacity	5.17 kg/s

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Table 22. Equipment characteristics evaluation of the biotechnological production process of resveratrol using WL as substrate.

Equipment	Number of units	Label	Equipment characteristic	
Heat sterilizer	4	ST-103	Input flux	92.39 m^3/h
Seed fermenter	1	SFR-103	Volume	6.55 m^3
Seed fermenter	1	SFR-104	Volume	45.77 m^3
Seed fermenter	1	SFR-105	Volume	65.84 m^3
Heat sterilizer	5	ST-101	Input flux	88.02 m^3/h
Fermenter	1	FR-101	Volume	213.17 m^3
Rotatory vacuum filter	4	RVF-102	Filter area	185.38 m^2
Storage tank	1	V-103	Volume	49.10 m^3
Rotatory vacuum filter	1	RVF-103	Filter area	153.21 m^2
Spray dryer	1	SDR-101	Drying capacity	35.07 kg/s

Table 23. Equipment characteristics evaluation of the biotechnological production process of resveratrol using ER as substrate.

Equipment	Number of units	Label	Equipment characteristic	
Plug flow reactor	1	PFR-101	Volume	2.05 m^3
Flash	6	V-102	Volume	19.99 m^3
Heat exchanger	4	HX-102	Exchange area	88.17 m^2
Belt filter	13	BF-101	Filter capacity	4.38 m^3/h
Heat exchanger	2	HX-103	Exchange area	65.28 m^2
Stirred reactor	2	R-101	Volume	372.7 m^3
Rotatory vacuum filter	10	RVF-101	Filter area	168.89 m^2
Heat sterilizer	8	ST-103	Input flow	99.34 m^3/h
Seed fermenter	1	SFR-103	Volume	281 L
Seed fermenter	1	SFR-104	Volume	1.59 m^3
Seed fermenter	1	SFR-105	Volume	7.09 m^3
Heat sterilizer	1	ST-101	Input flow	22.67 m^3/h
Fermenter	2	FR-101	Volume	573.31 m^3
Rotatory vacuum filter	10	RVF-102	Filter area	168.89 m^2
Storage tank	2	V-103	Volume	147.72 m^3
Rotatory vacuum filter	5	RVF-103	Filter area	182.81 m^2
Spray dryer	1	SDR-101	Drying flow	50.31 kg/s

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Table 24. Equipment characteristics evaluation of the biotechnological production process of resveratrol using CW substrate.

Equipment	Number of units	Label	Equipment characteristic	
Ultrafiltration	5	UF-101	Filtration area	197.04 m^2
Ultrafiltration	4	UF-102	Filtration area	194.71 m^2
Ultrafiltration	5	UF-103	Filtration area	175.19 m^2
Rotatory vacuum filter	2	RVF-101	Filtration area	53.08 m^2
Spray dryer	1	SDR-101	Drying capacity	13.51 kg/s
Pasteurizer	6	PZ-101	Input flow	35.88 m^3/h
Seed fermenter	1	SFR-103	Volume	0.28 m^3
Seed fermenter	1	SFR-104	Volume	1.59 m^3
Seed fermenter	1	SFR-105	Volume	7.09 m^3
Heat sterilizer	1	ST-101	Input flow	22.67 m^3/h
Fermenter	1	FR-101	Volume	52.01 m^3
Rotatory vacuum filter	1	RVF-102	Filtration area	165.29 m^2
Storage tank	1	V-103	Volume	2.80 m^3
Rotatory vacuum filter	1	RVF-103	Filtration area	9.30 m^2
Spray dryer	1	SDR-101	Drying capacity	0.99 kg/s

13.5.2 Environmental evaluation

13.5.2.1 S01-Vine pruning residues

The summary of the life cycle inventory data used for the development of the environmental assessment of S01- Vine Pruning is included in **Table 25**. All process-related inputs and outputs have been estimated from mass and energy balances.

Table 25. Main inventory data for the biotechnological valorization of VP residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	54.14	ton	Resveratrol	1	kg
Cellic CTec2	2.17	kg			
Dextrose	0.40	kg			
Ethanol	19.65	kg			
Peptone	0.41	kg	*Emissions to air*		
Sulfuric acid	0.48	kg	Carbon dioxide	1.32	kg
VP	318.98	kg	Acetic acid	3.40	kg
Water	1.41	m^3			
Yeast extract	1.11	kg	*Waste to treatment*		
Electricity/heat			Biomass	13.69	kg
Cooling water	146.7	m^3	Solid waste	187.9	kg
Steam	4.99	ton			
Electricity	478.1	kWh			

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Once the LCI was developed, the ReCiPe Midpoint methodology was applied to obtain the environmental profile of the valorization process (**Figure 18**). As can be seen, three main contributors were identified, with steam presenting the greatest environmental burden in most of the impact categories evaluated. The reason for this notable impact derives from the amount of steam required by FU, taking into account its production from fossil resources. On the other hand, it is worth mentioning that steam requirements have been partially reduced thanks to the anaerobic digestion of lignin and spent biomass, which means 83.42 kg steam/kg of resveratrol produced and, consequently, 12% less external steam. Electricity also contributes on the toxicity-related impact categories, namely FET, MET, HCT and HNCT, while the use of ethanol as a solubilization agent for resveratrol purification has a significant burden in the ME, LU and MRS impact categories. As for electricity, its production from fossil resources is the main reason for its contribution, while, in the case of ethanol, the related background activities necessary for its production (both material consumption and energy requirements) are the reason for its environmental burden on the above impact categories.

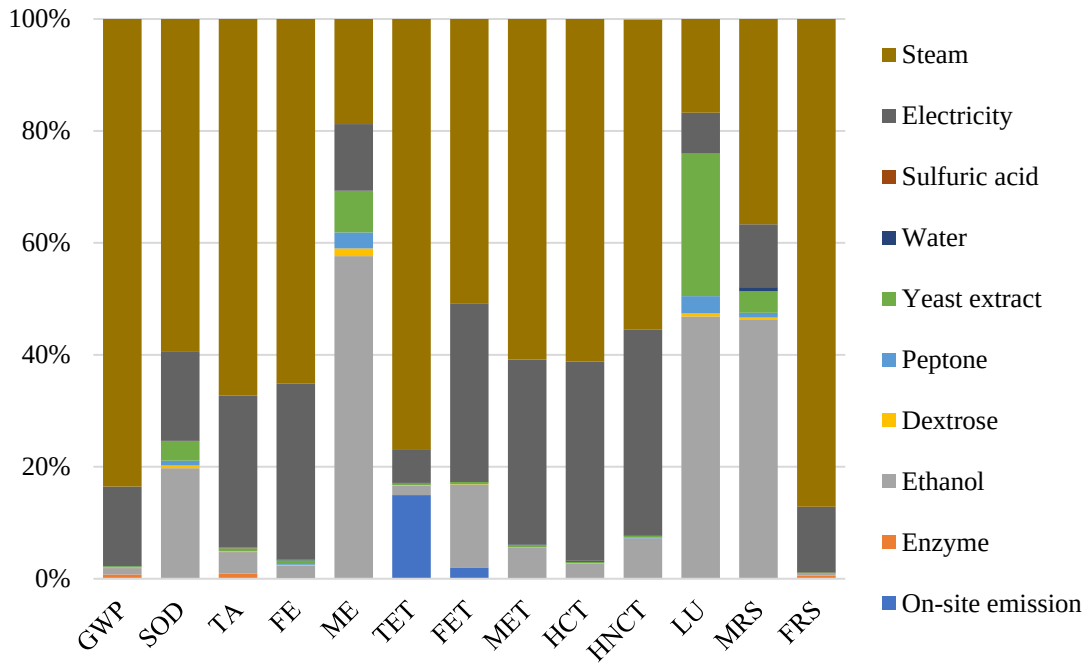

Figure 18. Environmental profile of resveratrol production using VP as substrate

13.5.2.2 S02- Grape must

The summary of the life cycle inventory data used of S02- Grape Must is included in **Table 26**, considering as functional unit the production of 1 kg of resveratrol. Avoiding the feedstock pretreatment stage implies a significant decrease in the thermal energy needs of the process, since the hydrothermal liquefaction stages, as well as temperature maintenance in enzymatic hydrolysis and post-chemical hydrolysis, necessary for the release of sugars from the VP, are highly demanding of this utility. Therefore, in this scenario, the environmental contribution of steam is irrelevant (**Figure 19**), being in this case electricity the one that carries a higher environmental load in most of the impact categories, except for the SOD, ME, LU and MRS categories. In those aforementioned impact categories, the use of peptone and yeast extract, used as nutrient source in the fermentation processes, have a higher environmental contribution, being that of peptone slightly higher.

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Table 26. Main inventory data for the biotechnological valorization of GM residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	4664	kg	Resveratrol	1	kg
Dextrose	6.98	kg			
Ethanol	0.05	kg			
Peptone	7.14	kg	*Emissions to air*		
GM	374.36	kg	Carbon dioxide	1.66	kg
Water	166.68	kg	Acetic acid	4.03	kg
Yeast extract	4.01	kg	*Waste to treatment*		
Electricity/heat			Biomass	3.22	kg
Cooling water	46.32	m^3	Solid waste	90.27	kg
Steam	36.29	kg			
Energy	268.38	kWh			

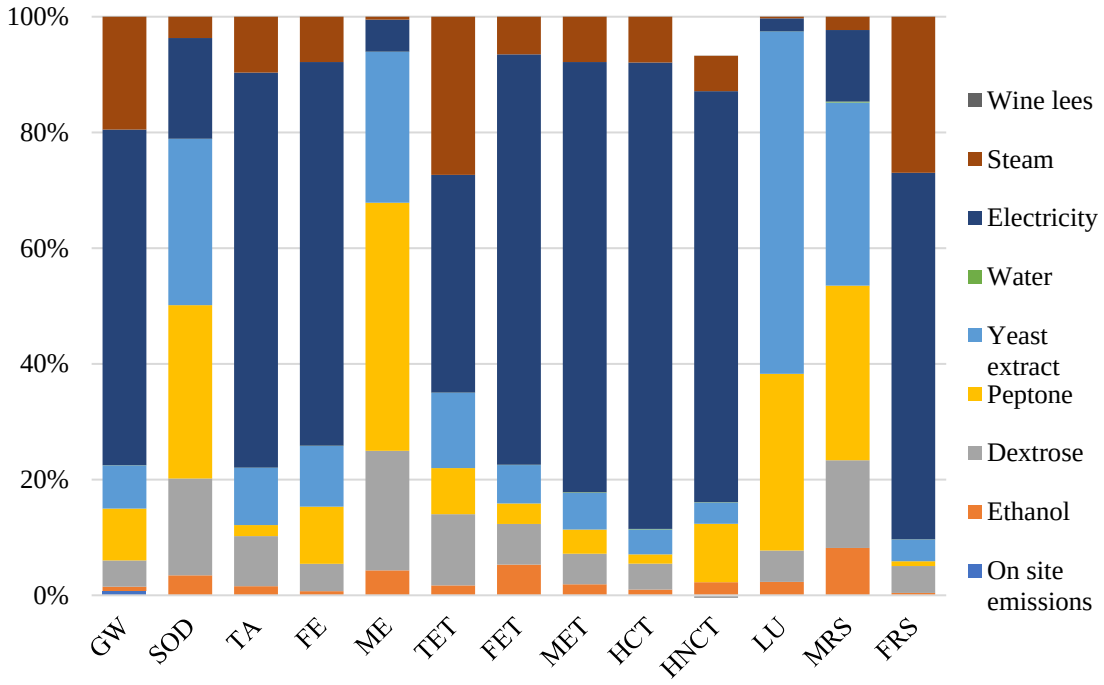

Figure 19. Environmental profile of resveratrol production using GM as substrate

13.5.2.3 S03- Wine lees

The gathered data of the life cycle inventory data used of S03- Wine lees is included in **Table 27**. **Figure 20** shows the environmental profile of the S03-WL valorization scenario, where it is observed that there is a greater distribution of impacts among the components that make up the life cycle inventory. However, it is still identified that the electrical requirements are those that make the greatest environmental contribution to the profile obtained in most of the impact categories, with the exception of 4: SOD, ME, LU and MRS, analogous to what was observed for Scenario S02. Once again, the formulation of the fermentation medium is the main cause of the environmental load of these four categories. On the other hand, it is observed in this profile that the contribution of steam is slightly higher than in the previous section. The reason for this variation, given the analogy between the processes, is due to the reduction in the

amount of resveratrol obtained, which implies a greater need for heat energy per unit kg of resveratrol produced.

Table 27. Main inventory data for the biotechnological valorization of WL residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Air	37.65	ton	Resveratrol	1	kg
Dextrose	31.49	kg			
Ethanol	7.74	kg			
Peptone	32.34	kg	*Emissions to air*		
WL	1276	kg	Carbon dioxide	5.71	kg
Water	724.92	kg	P-coumaric acid	0.61	kg
Yeast extract	20.51	kg	*Waste to treatment*		
Electricity/heat			Biomass	16.13	kg
Cooling water	201.8	m^3	Solid waste	76.29	kg
Steam	699.5	kg			
Energy	1172	kWh			

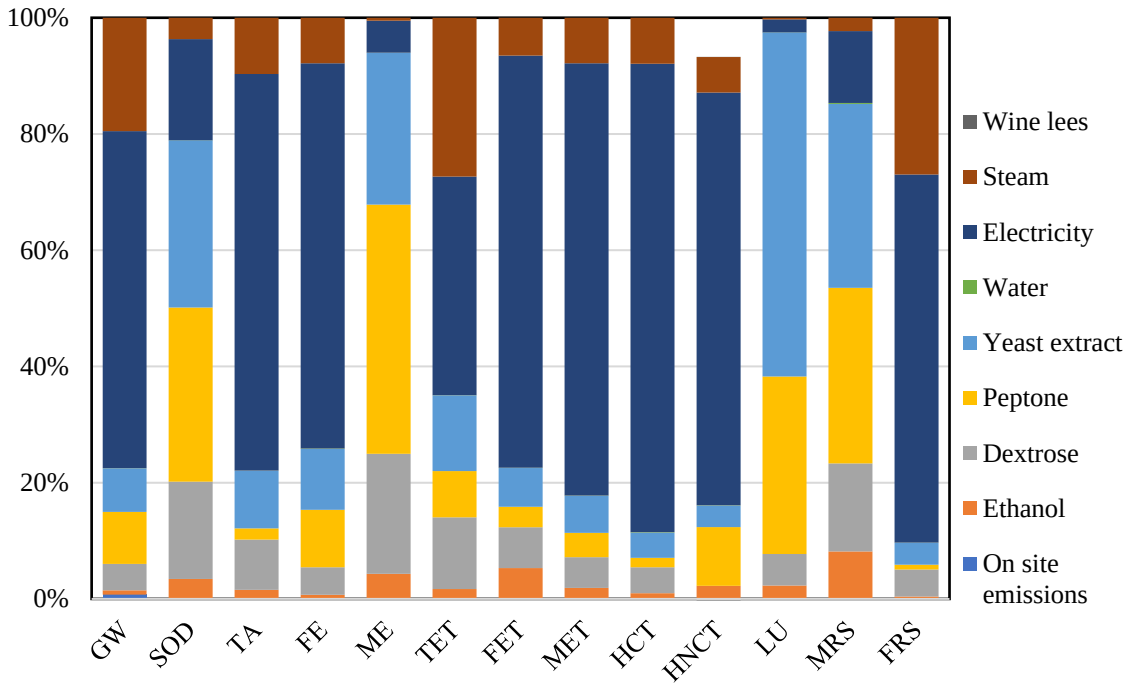

Figure 20. Environmental profile of resveratrol production using WL as substrate

13.5.2.4 S04- Eucalyptus residues

The life cycle inventory characteristic of the first valorization scenario, S04-ER, is included in **Table 28**. Process modelling was used for gathering all the input and output data, including emissions and waste streams.

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Table 28. Main inventory data for the biotechnological valorization of ER residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Cellic CTec2	2.33	kg	Resveratrol	1.00	kg
Glucose	0.73	kg			
Ethanol	20.09	kg			
Eucalyptus residues	0.49	ton			
Peptone	0.63	kg	*Emissions to air*		
Sulfuric acid	0.80	kg	Carbon dioxide	1.33	kg
Yeast extract	1.71	kg	Ethanol	1.69	kg
Water	0.93	m^3	Water vapour	47.45	L
			Waste to treatment		
Electricity/heat			Biomass	0.19	ton
Cooling water	7756	m^3	Wastewater	0.45	m^3
Steam	$8.18 \cdot 10^8$	kJ			
Energy	137.66	MWh			

Once the LCI has been developed, the ReCiPe Midpoint methodology has been used to obtain the environmental profile of S04-ER, depicted in **Figure 21**. As can be seen, two main contributors could be identified, with steam carrying the largest environmental load in the highest impact categories evaluated. The reason behind this huge impact is the result of the amount of steam required per procedure per batch (around $8.18 \cdot 10^5$ MJ/batch), which is produced from fossil energy sources. To decrease the steam requirements, the lignin content of ER and the biomass produced within the process are valorized through an anaerobic digestion, that allows to produce $3.25 \cdot 10^5$ MJ steam/batch. This recovery will imply about 40% reduction in external steam. Electricity requirements also have some contribution on the toxicity-related impact categories, namely GW, TET and FRS, while the use of enzymes for the pretreatment section has certainly a significant burden on the ME, LU and SOD impact categories. With respect to electricity, its production from fossil resources is the main reason for its contribution, while the related background activities required for their production of enzymes (mainly energy requirements) are the reason behind their environmental burdens on the above-mentioned impact categories.

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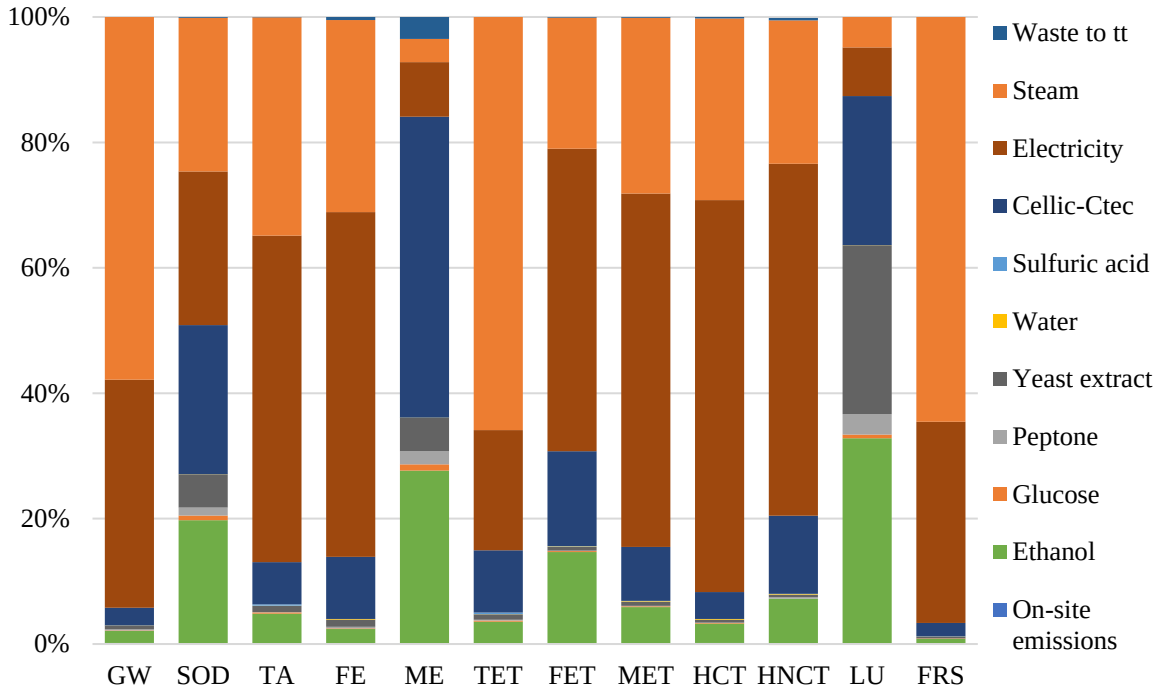

Figure 21. Environmental profile of resveratrol production using ER as substrate

13.5.2.5 S05- Cheese whey

The life cycle inventory data used of S05-CW is included in **Table 29**, considering as functional unit an entire batch process. In this case, not only resveratrol is obtained, but also a protein extract, which is considered as a co-product of the process, obtained as a power containing 57% w/w.

Table 29. Main inventory data for the biotechnological valorization of CW residues.

INPUTS FROM TECHNOSPHERE			OUTPUTS TO TECHNOSPHERE		
Cheese Whey	5.35	kton	Resveratrol	1	kg
Lactose	6.74	ton	*Co-product*		
Ethanol	19.86	ton	Protein powder 57% w/w	141	ton
Peptone	6.91	ton	*Emissions to air*		
Yeast extract	3.63	ton	Carbon dioxide	5.36	ton
Water	337	m^3	Ethanol	17.85	ton
			Water, vapor	8.47	ton
			Waste to treatment		
Electricity/heat			Biomass	36.43	ton
Cooling water	$7.41 \cdot 10^4$	m^3	Wastewater	$2.27 \cdot 10^3$	m^3
Steam	$1.42 \cdot 10^7$	MJ			
Electricity	562	MWh			

The environmental profile of the valorization of CW is depicted on **Figure 22.** The energy requirements of the process are the major contributors in most of the impact categories, with steam being the main hotspot, contributing more than 50% of the profile for the categories

related to GW, ecotoxicities, FRS and human health-related toxicities. On the other hand, as mentioned above, the impact derived from whey is important given its content in organic matter, promoting a significant contribution in the category of eutrophication, EM. In addition, since whey is a co-product with commercial value, the associated production process presents an associated impact, which also implies having certain significant impacts in the SOD, LU and MRS categories. On the other hand, as far as electricity is concerned, its contribution is lower compared to the previous process. The reason for this fact has a double justification: (1) pretreatment stage with a lower number of equipment and (2) the implementation of a pasteurization process using steam.

For this reason, the sensitivity analyses to be developed subsequently should focus on the reduction of steam consumption, or on replacing fossil resources to obtain it, as well as on improving the productive yield of the process, in order to obtain a greater volume of products per unit of raw material that enters the production system.

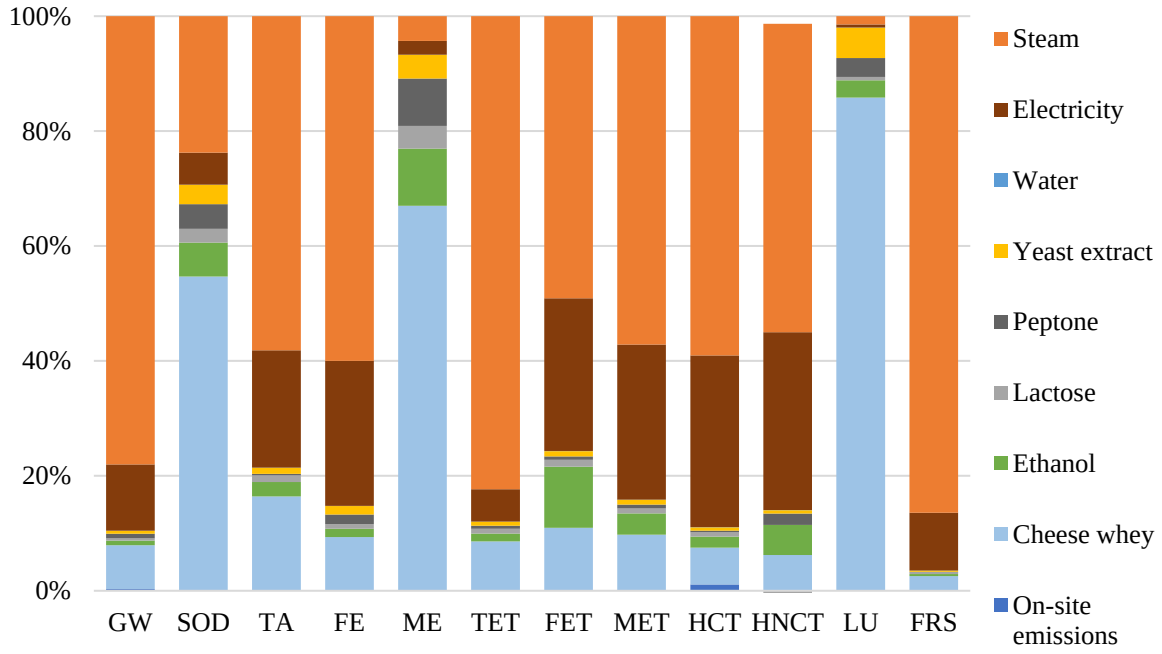

Figure 22. Environmental profile of resveratrol production using CW as substrate

13.5.3 Sensitivity assessments to reduce the environmental loads.

In order to reduce the environmental impact associated with the evaluated scenarios, sensitivity analyses have been carried out around the main critical points identified in the previous section. Consequently, the sensitivity analyses to be developed subsequently should focus on the reduction of steam consumption, or on the substitution of fossil resources to obtain steam, as well as on the improvement of the productive performance of the process. On the other hand, these sensitivity scenarios have been evaluated separately for each one of the valorization schemes.

13.5.3.1 S01- Vine pruning residues.

The main critical points identified for the S01-VP have been steam requirements, firstly, followed by electricity requirements and, in certain impact categories, ethanol, used for the solubilization of resveratrol for its purification. For this, the sensitivity analysis has been based

on the three components, and two approaches have been considered, on the one hand, the possibility of improving the productivity and efficiency of the process, which will lead to a reduction in the need for energy and material requirements, and on the other hand, by using renewable resources to obtain both steam and electricity, instead of using fossil resources for their production.

In the case of steam and electricity, a reduction in requirements of 20% has been estimated, which is considered feasible since the results of the laboratory scale approach have been extended and the degree of improvement is greater. On the other hand, as for ethanol, only a decrease on a 10% dose has been evaluated, due to the fact that the solubilization of resveratrol in this compound is important to achieve its adequate purification, and it is possible that the diminishment of the ethanol dose would alter the final quality of the product. With this in mind, **Figure 23** shows that the reduction of steam requirements leads to a better improvement of environmental loads in most of the impact categories evaluated. The only exception is observed for ME and LU, where it is the reduction of ethanol that provides the lowest impact. With respect to the reduction in electricity requirements, the reduction in impact is also notable, with the categories related to toxicity and eutrophication showing the greatest reduction.

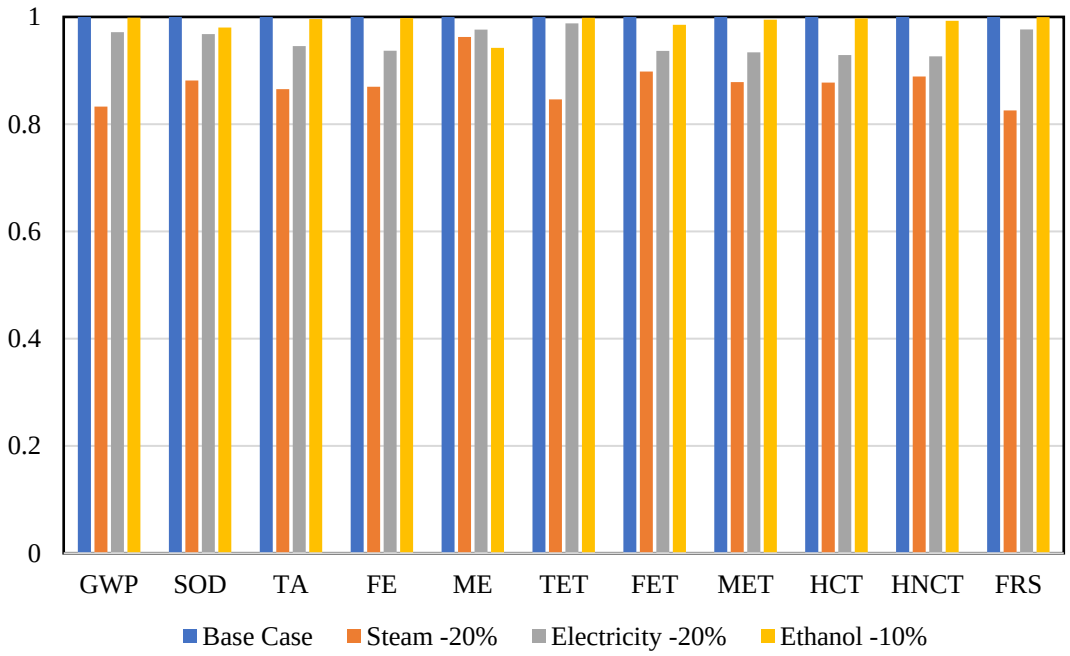

Figure 23. Sensitivity assessment of the environmental profile of VP valorisation for resveratrol production considering a reduction in steam and electricity use of 20% and in ethanol dosage of 10%.

Since the contribution of steam and electricity is so high, it has been considered to develop an additional sensitivity assessment, but in this case, based on the use of renewable energy resources. In this sense, **Figure 24** shows that the environmental loads of the process are significantly reduced in most impact categories by more than 30% for the GW, TA, FE, HTC and FRS when the resource for steam production is the burning of wood waste in a furnace with a capacity of 5000 kW, while for the case of renewable electricity, reductions in loads were estimated from 5% in the TET category to a maximum of 88% for the MRS, with respect to the base case scenario. In addition, another sensitivity analysis has been evaluated considering both steam and electricity from renewable resources, instead of considering each scenario separately,

for this case, a range of environmental load reduction from 12% to 98% is achieved, which shows the significant improvement of the environmental profile.

On the other hand, it is worth mentioning that in three impact categories, SOD, LU and HNCT, the impact was improved. The fact that renewable resources are used implies a greater impact on land use, given the need to use land to obtain this energy. For example, in the case of steam from hardwood, it implies the use of extensive areas for forest management. In the case of SOD, the production of the equipment necessary for the development of renewable energy production and the derived on-site emission have the most acute influence. Finally, in the case of HNCT, the impact ratio is only slightly the same as for SOD.

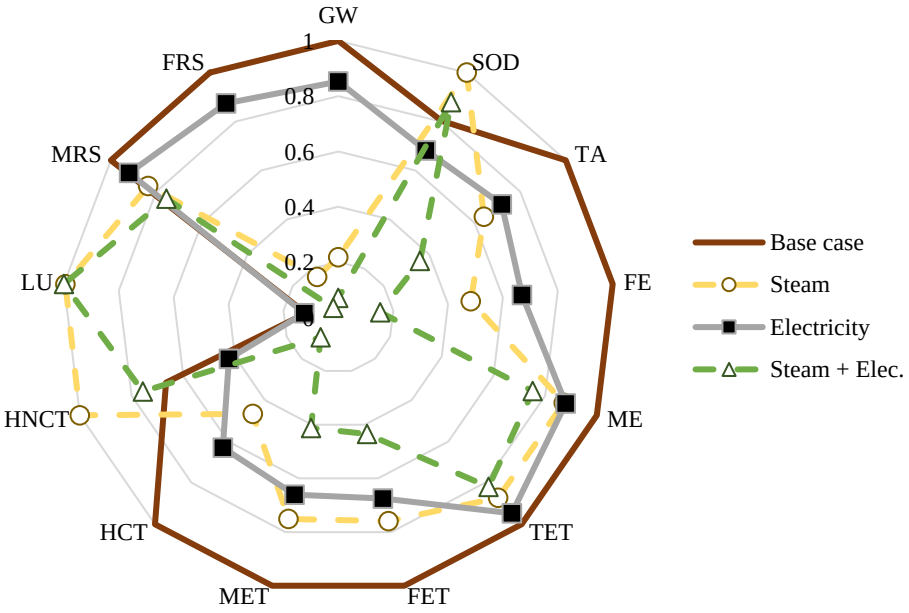

Figure 24. Sensitivity assessment of the environmental profile of VP valorisation for resveratrol production considering the use of renewable resources for electricity and steam production.

13.5.3.2 S02- Grape must

The hotspots identified for the S02-GM have been the electricity requirements and also some significant contribution of the peptone used as nitrogen source in the formulation of the culture medium. For this purpose, the sensitivity analysis has been based on (1) the reduction of the chemicals used for the culture medium, which is expected to be achieved by improving the yield and productivity of the process (the fact that it is based on a laboratory scale process actually implies a significant improvement after scaling up to an industrial process capacity), (2) the decrease of electricity requirements by increasing productivity or the improvement of the equipment used for the process by increasing its efficiency and (3), as in the previous scenario the use of renewable resources for energy production actually implies a significant reduction of the environmental load, the use of renewable resources for their production has also been evaluated.

The sensitivity results obtained are depicted in **Figure 25**. As expected, the use of electricity from renewable resources implies the highest reduction in environmental load in all impact categories, with the exception of the TET and LU impact categories, where the scores obtained are not so low compared to those of the other categories. The range of environmental impact reduction ranges from 6% for the ME category to 84% for HCT, with respect to the baseline scenario, when renewable resources are used. The percentage decrease is significantly

reduced for the case of reducing the amount of electricity required by 20%, from 1% to 18% for the ME and HCT impact categories, respectively. Finally, for the scenario based on reducing the peptone dose, the scores are the lowest, with the highest percentage reduction in the ME impact category, reaching 9%.

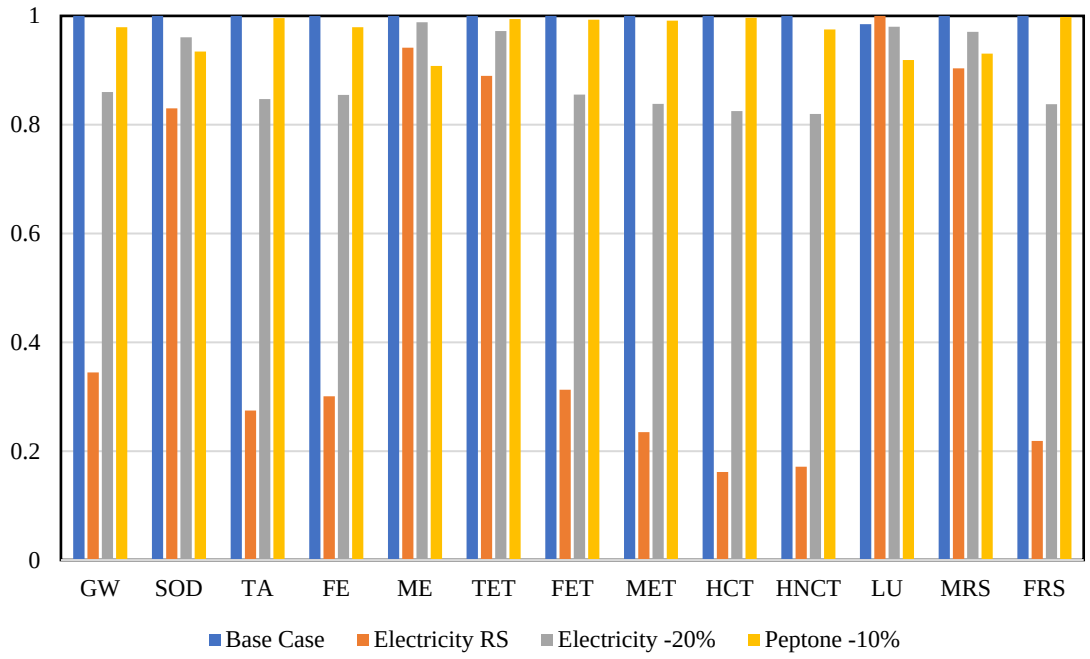

Figure 25. Sensitivity assessment of the environmental profile of GM valorisation for resveratrol production considering a 20% reduction in electricity use, the use of renewable energy resources and a 10% reduction in peptone dosage.

13.5.3.3 S03- Wine lees

An analogous trend on the reduction of impact contribution loads is obtained when evaluating the sensitivity analysis of the wine lees valorization scenario (**Figure 26**), given the similarity between the process scheme of the S02-Grape must scenario. The scenarios evaluated are the same as the previous one, considering renewable resources for electricity production, a 20% reduction in its requirements and a 10% reduction in peptone addition.

As expected, the renewable nature of the electricity leads to a decrease of environmental loads in the order of 5% to 77%. In this case, the reduction is slightly lower than in the previous case, since a smaller amount of resveratrol is obtained. In the case of the 20% on decreasing electricity requirements, the reduction goes from 1% in the ME category to 16% in the impact categories related to human toxicity. As in the previous case, the one with the lowest improvement profile is the diminishment in the amount of peptone, reaching a reduction of 9% in the case of the ME impact category. Therefore, it could be concluded that process improvement actions should focus on opting for the use of renewable energies and improving process efficiency, although a more sustainable production model would be promoted when it is decided to use alternative energy sources.

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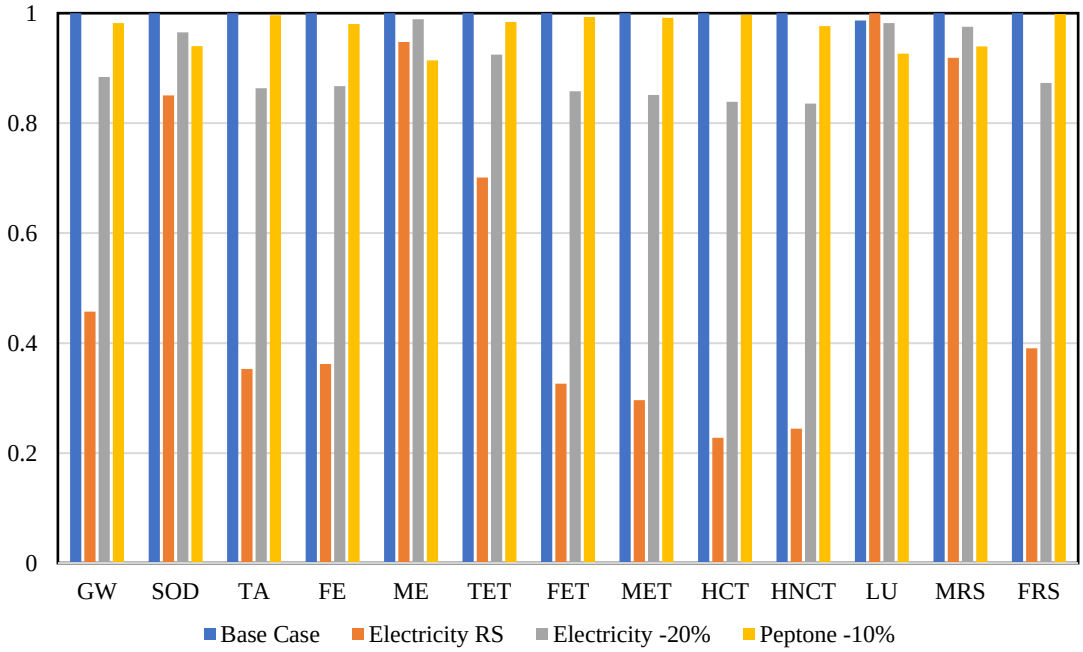

Figure 26. Sensitivity assessment of the environmental profile of WL valorisation for resveratrol production considering a 20% reduction in electricity use, the use of renewable resources for electricity production and a 10% reduction in peptone addition.

13.5.3.4 S04- Eucalyptus residues

The main hotspots identified for S04-ER have been steam requirements, followed by cheese whey in some impact categories, such as ME, LU and SOD, and almost followed by electricity requirements. Since significant contributors on the environmental profile have been detected, a sensitivity assessment has been proposed with the objective of providing improvement scenarios with reduced environmental burdens.

In the case of steam requirements, the first scenario has been based on the valorization of the lignin and the biomass from the fermentation stage. This valorization is developed through the inclusion of an anaerobic digestion unit, which allows to obtain $3.25 \cdot 10^5$ MJ steam/batch, which is a significant amount that allows to reduce by almost half the steam requirements based on fossil resources. As can be seen in **Figure 27**, this valorization implies a reduction of about 8% for ecotoxicity categories, 13% for GW and 26% for FRS impact category, which is the highest reduction value obtained when compared to the base scenario. The other alternative to be evaluated is the use of steam from renewable resources, thus avoiding the depletion and environmental consequences of fossil fuel use. In this case, the reduction values increase, as expected, with a reduction of about 25% for the TA, FE and HCT impact categories, 53% for GW and 61% for the FRS impact category. On the other hand, it is worth mentioning that the using steam from renewable resources could imply a greater impact on other impact categories, such as LU, SOD and HCNT, given the associated production process, which involves greater land occupation than the use of fossil sources and certain emissions that could cause non-carcinogenic impacts on human health and ozone depletion. However, given the significant benefits achieved by this modification in the production source, these certain greater impacts are certainly offset.

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With respect to electricity, a similar approach has been considered, as the use of renewable resources for its production is analyzed. In this regard, significant reduction loads are obtained in all the impact categories when comparing to the base case. The range of improvement goes from an 8% of reduction of the ME impact category to 60% on the HCT category, with a 34% of improvement over the GW, a mean reduction of 38% over the ecotoxicity-related categories and a 31% for the case of the fossil resources consumption (FRS). Considering these values, it could also be concluded that the substitution of the use of fossil resources by the use of renewable resources implies a substantial improvement in the environmental profile of the process.

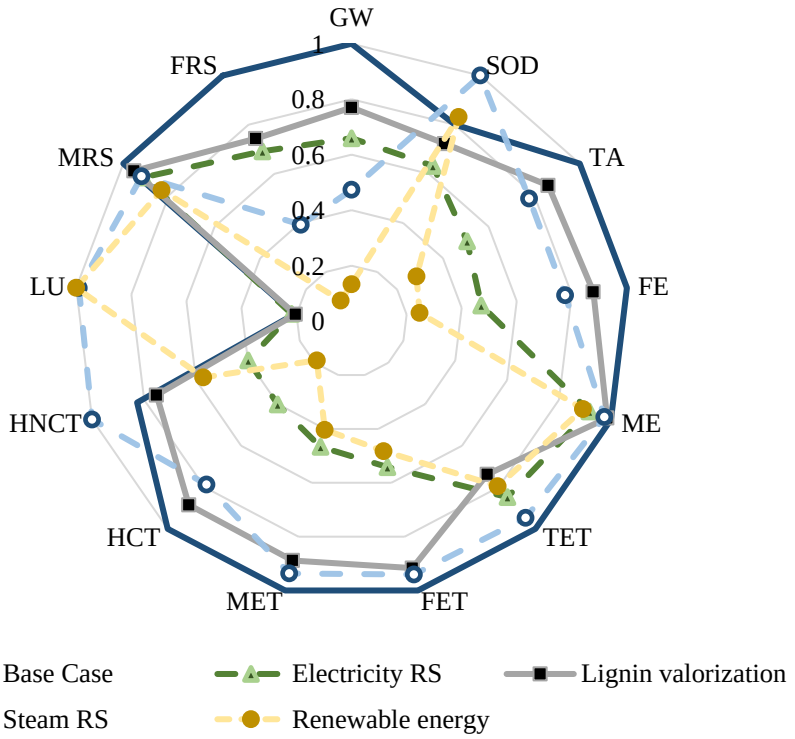

Figure 27. Sensitivity assessment of the environmental profile of ER valorization for resveratrol production considering the use of renewable resources for the production of electricity and steam.

13.5.3.5 S05- Cheese whey

The hotspots for the S05-CW scenario are electricity needs and, to a lesser extent, cheese whey. For this, the sensitivity analysis has been based on (1) the reduction of electricity needs by 20%, (2) the use of renewable resources for electricity production, (3) the reduction of the amount of cheese whey used and (4) the combined use of renewable resources for electricity production and the reduction of the cheese whey input flow.

As expected, the use of electricity from renewable resources implies the lowest environmental loads, in all impact categories, with the exception of the TET and LU impact categories, where the scores obtained are not as low compared to the others (**Figure 28**). The range of environmental impact reduction ranges from 6% for the ME category to 84% for HCT, with respect to the baseline scenario, when renewable resources are used. The percentage decrease is significantly diminished in the case of reducing the amount of electricity required by 20%, from 1% to 18% for the ME and HCT impact categories, respectively. A sensitivity

assessment of cheese whey has also been considered, evaluating a reduction of its input by 20%, based on the fact that a higher productivity and efficiency of the process could be obtained, so that a lower amount of cheese whey input will be necessary to obtain the same amount of product as in the base scenario. In this sense, significantly reduced impacts are obtained for the SOD, ME and LU impact categories, for which a reduction of 11%, 13% and 17%, respectively, is achieved.

When considering all the improved sensitivity scenarios, an optimized one has been evaluated, for which impact reductions are obtained in a range from 10% for the FRS impact category to 30% for the impact categories related to human toxicity, namely HCT and HNCT. The latter sensitivity scenario is the one with the best environmental profile.

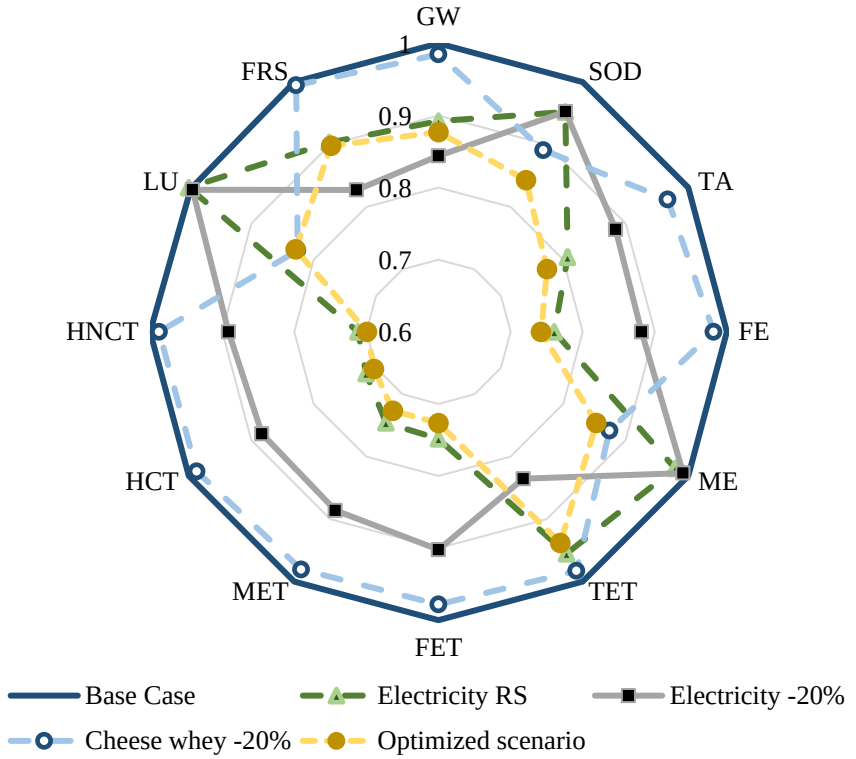

Figure 28. Sensitivity assessment of the environmental profile of CW valorization for resveratrol production considering a reduction on the use of electricity by 20%, the use of renewable resources for electricity production and on cheese whey input by 20%.

13.5.4 Techno-economic analysis

The techno-economic scores obtained for the two proposed valorization scenarios are represented in **Table 34**, including equipment costs, fixed capital, variable operating costs, expected revenues and estimated minimum sales prices of the main product to guarantee the viability of the process. As can be seen, the pretreatment stage has a notable influence on the total investment of the S01-VP and S04-ER waste valorization scenario, since its amount is almost double in comparison to the other scenarios, mostly derived from equipment acquisition costs. On the other hand, the need to include high temperature and pressure operating conditions, as is the case of hydrothermal pretreatment of olive pruning and eucalyptus waste

prior to its enzymatic and acid hydrolysis, implies a higher need for labor costs. Although, in the case of the cost of materials and utilities its value is somewhat lower, with the exception of S05-CW scenario, the reason for this is due, firstly, to the use of lignin and fermentation biomass for obtaining heat energy, which reduces the external need for steam, which is one of the higher cost utilities and, secondly, to the higher resveratrol extraction yield, which certainly implies that the material costs are also somewhat lower.

Therefore, through the economic evaluation, taking into account the annual operating costs and expected revenues, the minimum selling price (MSP) of resveratrol for the S01-VP process to be economically viable amounts to 380.28 €/kg, while for the case of the S04-ER the MSP is increased to 531.12 €/kg. Regarding this item, the S02-GW scenario is the one with the lowest MSP, amounting to 193.82 €/kg which coverts it in the most promising waste valorization alternative, not only because of this, but also given the fact that total investment costs, which are the lowest, and for the expected revenues that could be obtained from the sale of the resveratrol obtained, which are the highest, however it should be mentioned that higher labor, materials and utilities expenditures has been obtained, but those are compensated by the other economic parameters required to provide the final MSP score. Lastly, in the case of the S05-CW, given the low production capacity of resveratrol, its MSP is the highest one, amounting to 1,747 €/kg, in fact it is almost 10 times higher to that of S02-GM, 6 times higher with respect to S01-VP and 3 times in comparison to S04-ER, being S03-WL scenario the one with the closest one, but still significantly lower.

Table 34. Economic evaluation parameters of the biotechnological production process of resveratrol using the different substrates.

Economic Parameters	S01-VP	S02-GM	S03-WL	S04-ER	S05-CW
Total Investment [€]	42,239,000	19,203,000	20,750,000	41,325,000	24,400,000
Equipment cost [€]	9,537,000	3,131,000	3,380,000	8,780,000	5,220,000
1. Total Plant Direct Cost [€]	23,696,000	10,436,000	11,277,000	21,923,000	12,984,000
2. Total Plant Indirect Cost [€]	13,033,000	6,262,000	6,766,000	12,058,000	7,141,000
Labor Cost [€/year]	1,172,884	1,580,048	2,190,753	1,154,533	787,229
Material Cost [€/year]	80,854	1,673,071	2,395,819	74,435	22,661
Utilities Cost [€/year]	2,055,000	5,837,650	7,665,123	1,967,994	275,094
Annual Operation Cost [€/year]	8,328,000	12,740,047	16,190,753	7,886,000	3,862,000
Revenues [€/year]	19,709,313	37,924,464	11,125,097	13,363,691	2,263,660
MSP [€/kg Resveratrol]	380.28	193.82	882.36	531.12	1,747.22

On the other hand, in order to evaluate whether these sales prices obtained are within the range of resveratrol sales prices, a bibliographic review of its sales prices has been carried out, taking into account that the resveratrol obtained in the scenarios has a purity of 95%. According to BOCSCI Inc, a laboratory chemical supplier of bulk compounds for the pharmaceutical, agrochemical and biotechnology industries, the purchase price amounts to 9,353 €/kg. Another company is BULK, which is based on the sale of foods, considers that the selling price of resveratrol should be around 1,500 €/kg, while for Sigma Aldrich is 1,784 €/kg. Since these companies supply resveratrol for a laboratory level production for individual intake, it has been assumed that the selling price of this compound could be halved, thus obtaining a selling price

range between 750-4,677 €/kg. Considering the average value, 2713 €/kg, all the valorization scenarios are below, being the S02-GM valorization a process scheme that allows to increase the sale value in a higher quantity, and therefore to be able to generate a significant volume of profit above the market average, being thus the most promising alternative.

13.5.5 Comparison between scenarios

As in the case of the techno-economic analysis, a comparison has also been made between the three process scenarios from an environmental perspective, considering the scores obtained by applying the Midpoint and Endpoint calculation methodologies. It is worth mentioning that this comparison is developed for the base case scenarios and not for those improved by the sensitivity analysis.

In this regard, **Table 35** includes the environmental scores obtained for each impact category and process scenario, highlighting in bold the process alternative that entails the highest environmental load in each impact category. For mostly all the impact categories, the S02-GM scenario is the one with the lowest environmental load, given its higher resveratrol productivity, thus leading to a lower impact per kg of product obtained, with the exception of SOD, ME, TET and LU impact categories, for which the S04-ER valorization is the one with the lowest scores.

Table 35. Environmental parameters obtained by performing the ReCiPe MidPoint methodology of the biotechnological production process of resveratrol using the different side streams. Functional unit: 1 kg of resveratrol

Impact category	Unit	S01-VP	S02-GM	S03-WL	S04-ER	S05-CW
GW	kg CO_2 eq	$1.30 \cdot 10^{3}$	$1.48 \cdot 10^{2}$	$7.81 \cdot 10^{2}$	$7.95 \cdot 10^{2}$	**$1.89 \cdot 10^{3}$**
SOD	kg CFC_{11} eq	$4.48 \cdot 10^{-4}$	$2.04 \cdot 10^{-4}$	$1.01 \cdot 10^{-3}$	$4.58 \cdot 10^{-4}$	**$1.51 \cdot 10^{-3}$**
TA	kg SO_2 eq	3.60	0.72	3.51	2.93	**5.63**
FE	kg P eq	0.21	0.05	0.24	0.19	**0.31**
ME	kg N eq	0.04	0.04	0.19	$7.55 \cdot 10^{-2}$	**0.22**
TET	kg 1.4-DCB	$1.98 \cdot 10^{3}$	$4.84 \cdot 10^{2}$	$7.78 \cdot 10^{2}$	$9.74 \cdot 10^{2}$	**$2.49 \cdot 10^{3}$**
FET	kg 1.4-DCB	6.24	1.54	6.84	6.42	**8.78**
MET	kg 1.4-DCB	8.49	1.94	9.23	7.77	**12.24**
HCT	kg 1.4-DCB	11.80	2.70	12.80	10.54	**16.67**
HNCT	kg 1.4-DCB	$3.02 \cdot 10^{2}$	69.24	$3.32 \cdot 10^{2}$	$3.09 \cdot 10^{2}$	**$4.17 \cdot 10^{2}$**
LU	m^2a crop eq	49.10	76.84	$3.38 \cdot 10^{2}$	70.20	**$7.58 \cdot 10^{2}$**
FRS	kg oil eq	$4.36 \cdot 10^{2}$	35.20	$1.97 \cdot 10^{2}$	$2.48 \cdot 10^{2}$	**$5.94 \cdot 10^{2}$**

Given the low productivity of the process in the production of resveratrol, as well as the consumption of energy resources and chemicals for the fermentation and purification phase of the final product, the S05-cheese whey valorization scenario is the one with the highest environmental contribution in most of the impact categories studied compared to the other two valorization scenarios evaluated. It is followed by the scenarios of S03-wine lees and S01- vine pruning, as it has the highest second loads. In fact, to show the degree of significant increase in impact, the values obtained have been normalized between 0 and 1, shown in **Figure 29**, where it can be seen that the impact caused by the S05 scenario is significantly higher in comparison to that of S02, the lowest impactful alternative, as in all the impact categories its environmental

contribution is over 80% higher. Therefore, it can be stated that the S05 scenario is the least favorable and that, possibly, for its better use and lower environmental impact, another valorization strategy should be chosen.

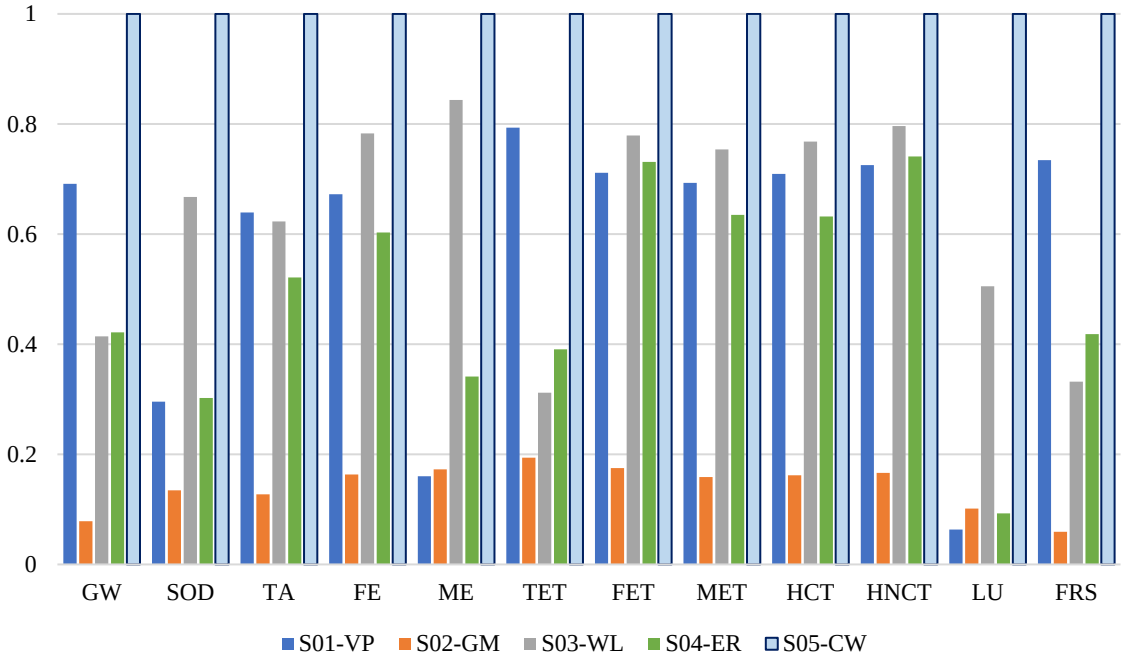

Figure 29. Comparison of the environmental loads of the assessed scenarios using the ReCiPe MidPoint methodology considering as functional unit 1 kg of resveratrol produced.

Figure 30 represents the ReCiPe Endpoint scores, providing 3 damage categories (human health, resources and ecosystems), which allows a global view of the impacts related to each scenario, considering both sensitivity scenarios, evaluating the use of renewable energy as resource for fulfill energy requirements, thus being represented with the acronym "ER" in the figure, and the base case, "BC", ones. As can be seen, there is an analogy between the results obtained for the base case with respect to the study under the ReCiPe MidPoint methodology, where the use of GM as raw material is again the one with the lowest environmental contribution and the use of CW the one with the highest impact on the environment.

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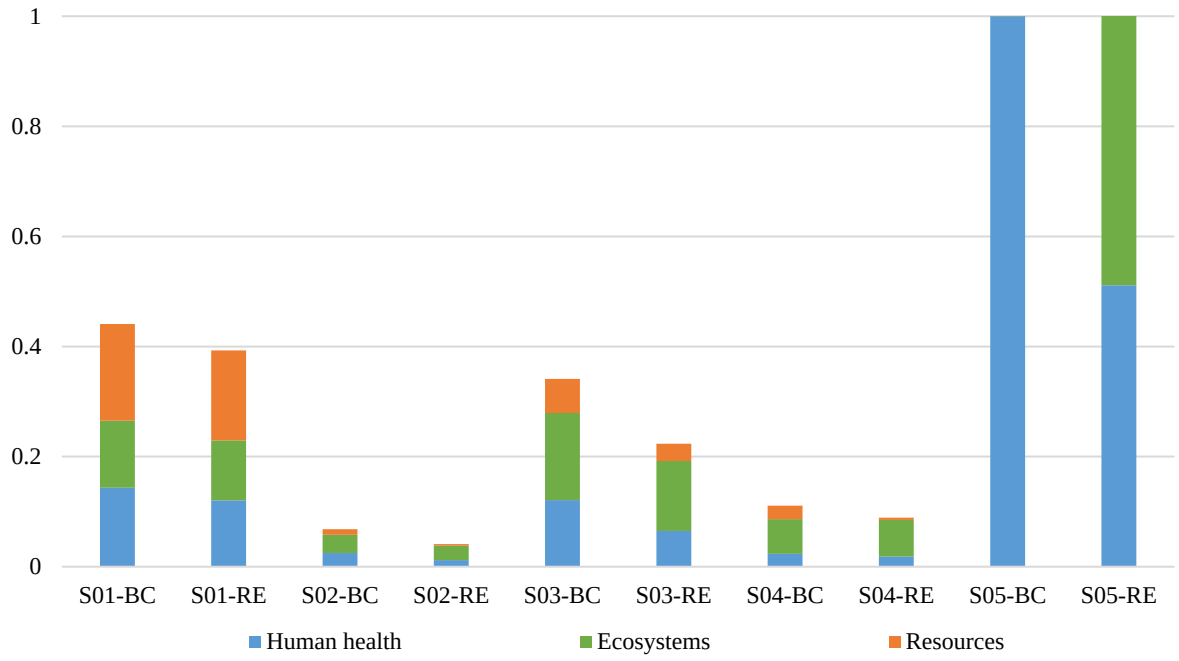

Figure 30. Comparison of the environmental loads of the assessed scenarios using the ReCiPe EndPoint methodology.

On the other hand, in order to be aware of the damage potential of its scenario, **Figure 31** is depicted, including S01, S02, S03 and S04 scenarios, and leaving behind the S05 given its huge environmental loads in comparison. The most important outcome obtained by the comparison of BC and ER improved scenarios is that the option for renewable energy sources significantly reduces the damage potential single score of the scenarios, specifically 49% for the S02, 44% for the S03 and 20% for S04 scenarios, achieving only a 15% of reduction for the S01 valorization alternative, which is the lowest one obtained. On the other hand, regardless of the damage category that is highly affected is the one of human health, that represents a total contribution over the damage potential of 89%, 86%, 87% and 83% for S01, S02, S03 and S04 scenarios, respectively.

Besides, looking for identify the best alternative, from an environmental perspective, it could be observed that the valorization of grape must for resveratrol production (S02-GM) is the most promising scenario also from an EndPoint perspective, followed by the eucalyptus residues one (S04-ER), as the damage potential of those alternatives are significantly lower to that obtained for vine pruning valorization (S01-VP) and somewhat inferior to the ones obtained for the wine less (S03-WL) production scheme.

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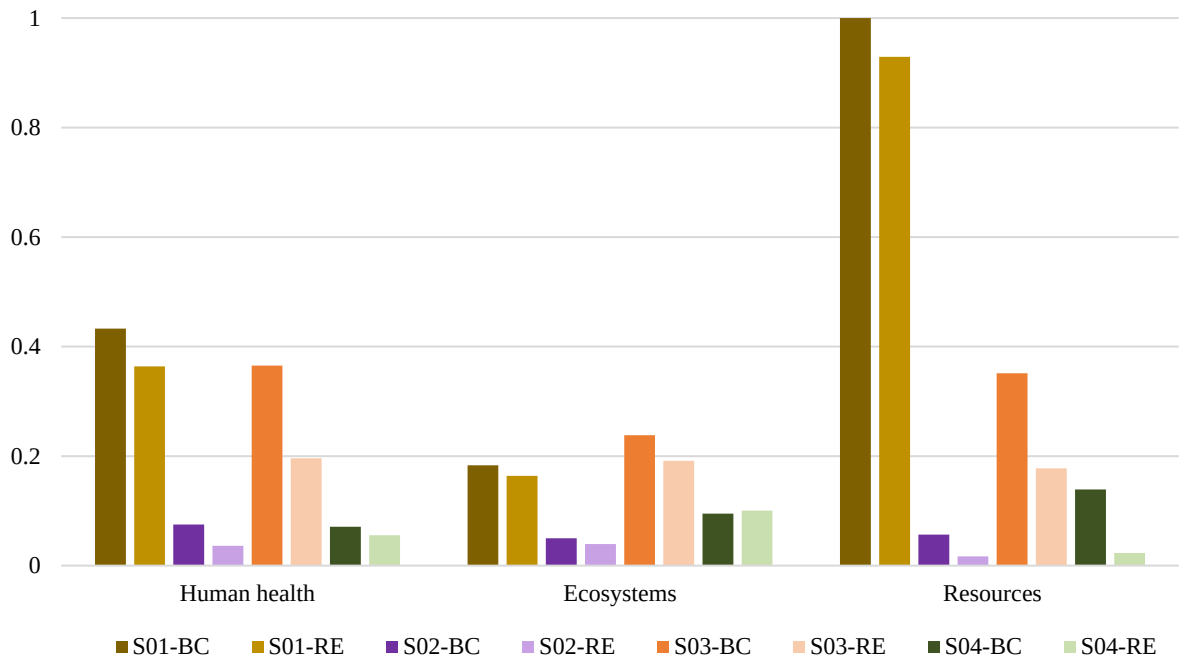

Figure 31. Comparison of the environmental loads of the assessed scenarios using the ReCiPe EndPoint methodology.

13.6 Eco-efficiency analysis for the five scenarios

With the aim of running an additional analysis method for the comparison of scenarios, the eco-efficiency analysis (EEA) methodology has been used. In accordance with the guidelines available in the international standard ISO 14046, the indices considered for the evaluation are associated with the economic and environmental pillars, being the costs and production capacity, those integrated in the economic aspect, and the impact loads obtained by the LCA methodology those used for the environmental approach. The EEA index values obtained are shown in **Table 32**. One way to represent the interrelationship between the environmental impacts and economic aspects of a process alternative is through eco-efficiency analysis. So far, the results have shown a greater adequacy in the environmental perspective in the case of cheese whey valorization, when it is contemplated to select as functional unit the total products obtained, However, by focusing on the exclusive production of resveratrol, the impacts associated with the valorization of eucalyptus residues are lower. Regarding the economic analysis, it has been observed that opting for the eucalyptus waste valorization scheme implies lower associated costs, as well as a lower minimum selling price of resveratrol to favor economic viability.

Given the above and the variation in the results obtained an eco-efficiency analysis is included, taking into account both WSP and operating costs and production capacity, all in comparison with the environmental loads obtained for each impact category and alternatives. In this approach, the main results obtained for the ratios are presented in **Table 32**, and for its effective comparison**, Figures 32, 33, 34** have been prepared, where it can be observed which alternative is characterized as eco-efficient (green region), as not eco-efficient (red region) or in an intermediate situation (yellow region). It is worth mentioning that the figures not only represent the base case study, but also the results optimized through the development of sensitivity analysis of the most contributing variables on the profile.

Table 32. EEA indexes obtained for S01- Vine pruning, S02- Grape must, S03- Wine lees, S04- Eucalyptus residues and S05-Cheese whey scenarios. Acronym EI refers to Environmental Impact.

Index	**€/ impact**					**€/ impact**					**kg products / impact**				
Variables	Minimum selling prince/EI					Production costs/EI					Production capacity/EI				
	S-01	*S-02*	*S-03*	*S-04*	*S-05*	*S-01*	*S-02*	*S-03*	*S-04*	*S-05*	*S-01*	*S-02*	*S-03*	*S-04*	*S-05*
GW	$6.73 \cdot 10^{-6}$	$8.20 \cdot 10^{-6}$	$1.56 \cdot 10^{-6}$	$8.96 \cdot 10^{-8}$	$8.44 \cdot 10^{-7}$	$4.61 \cdot 10^{4}$	$5.62 \cdot 10^{4}$	$1.07 \cdot 10^{4}$	$4.17 \cdot 10^{2}$	$2.64 \cdot 10^{1}$	$5.54 \cdot 10^{-3}$	$6.75 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$5.28 \cdot 10^{-5}$	$6.84 \cdot 10^{-6}$
SOD	$1.94 \cdot 10^{1}$	5.97	1.20	$1.94 \cdot 10^{-2}$	1.47	$1.33 \cdot 10^{11}$	$4.09 \cdot 10^{10}$	$8.24 \cdot 10^{9}$	$9.02 \cdot 10^{7}$	$4.59 \cdot 10^{7}$	$1.59 \cdot 10^{4}$	$4.91 \cdot 10^{3}$	$9.90 \cdot 10^{2}$	$1.14 \cdot 10^{1}$	$1.19 \cdot 10^{1}$
TA	$2.40 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$	$3.46 \cdot 10^{-4}$	$1.39 \cdot 10^{-5}$	$2.29 \cdot 10^{-4}$	$1.65 \cdot 10^{7}$	$1.16 \cdot 10^{7}$	$2.37 \cdot 10^{6}$	$6.45 \cdot 10^{4}$	$7.15 \cdot 10^{3}$	1.98	1.40	$2.85 \cdot 10^{-1}$	$8.18 \cdot 10^{-3}$	$1.85 \cdot 10^{-3}$
FE	$4.14 \cdot 10^{-2}$	$2.40 \cdot 10^{-2}$	$5.01 \cdot 10^{-3}$	$3.47 \cdot 10^{-4}$	$3.59 \cdot 10^{-3}$	$2.84 \cdot 10^{8}$	$1.64 \cdot 10^{8}$	$3.43 \cdot 10^{7}$	$1.61 \cdot 10^{6}$	$1.12 \cdot 10^{5}$	$3.41 \cdot 10^{1}$	$1.97 \cdot 10^{1}$	4.12	$2.04 \cdot 10^{-1}$	$2.91 \cdot 10^{-2}$
ME	$2.38 \cdot 10^{-1}$	$3.18 \cdot 10^{-2}$	$6.51 \cdot 10^{-3}$	$1.30 \cdot 10^{-4}$	$8.88 \cdot 10^{-3}$	$1.63 \cdot 10^{9}$	$2.18 \cdot 10^{8}$	$4.46 \cdot 10^{7}$	$6.05 \cdot 10^{5}$	$2.78 \cdot 10^{5}$	$1.96 \cdot 10^{2}$	$2.62 \cdot 10^{1}$	5.36	$7.67 \cdot 10^{-2}$	$7.20 \cdot 10^{-2}$
TET	$4.41 \cdot 10^{-6}$	$2.51 \cdot 10^{-6}$	$1.56 \cdot 10^{-6}$	$3.16 \cdot 10^{-8}$	$6.88 \cdot 10^{-7}$	$3.03 \cdot 10^{4}$	$1.72 \cdot 10^{4}$	$1.07 \cdot 10^{4}$	$1.47 \cdot 10^{2}$	$2.15 \cdot 10^{1}$	$3.63 \cdot 10^{-3}$	$2.07 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$1.86 \cdot 10^{-5}$	$5.58 \cdot 10^{-6}$
FET	$1.37 \cdot 10^{-3}$	$7.91 \cdot 10^{-4}$	$1.78 \cdot 10^{-4}$	$8.83 \cdot 10^{-6}$	$1.05 \cdot 10^{-4}$	$9.37 \cdot 10^{6}$	$5.43 \cdot 10^{6}$	$1.22 \cdot 10^{6}$	$4.11 \cdot 10^{4}$	$3.27 \cdot 10^{3}$	1.13	$6.51 \cdot 10^{-1}$	$1.46 \cdot 10^{-1}$	$5.21 \cdot 10^{-3}$	$8.47 \cdot 10^{-4}$
MET	$1.01 \cdot 10^{-3}$	$6.25 \cdot 10^{-4}$	$1.32 \cdot 10^{-4}$	$6.53 \cdot 10^{-6}$	$8.63 \cdot 10^{-5}$	$6.94 \cdot 10^{6}$	$4.28 \cdot 10^{6}$	$9.02 \cdot 10^{5}$	$3.03 \cdot 10^{4}$	$2.70 \cdot 10^{3}$	$8.34 \cdot 10^{-1}$	$5.14 \cdot 10^{-1}$	$1.08 \cdot 10^{-1}$	$3.85 \cdot 10^{-3}$	$6.99 \cdot 10^{-4}$
HCT	$7.26 \cdot 10^{-4}$	$4.50 \cdot 10^{-4}$	$9.49 \cdot 10^{-5}$	$7.32 \cdot 10^{-6}$	$6.36 \cdot 10^{-5}$	$4.98 \cdot 10^{6}$	$3.09 \cdot 10^{6}$	$6.50 \cdot 10^{5}$	$3.40 \cdot 10^{4}$	$1.99 \cdot 10^{3}$	$5.98 \cdot 10^{-1}$	$3.70 \cdot 10^{-1}$	$7.81 \cdot 10^{-2}$	$4.31 \cdot 10^{-3}$	$5.16 \cdot 10^{-4}$
HCNT	$2.83 \cdot 10^{-5}$	$1.75 \cdot 10^{-5}$	$3.66 \cdot 10^{-6}$	$1.38 \cdot 10^{-7}$	$2.17 \cdot 10^{-6}$	$1.94 \cdot 10^{5}$	$1.20 \cdot 10^{5}$	$2.51 \cdot 10^{4}$	$6.42 \cdot 10^{2}$	$6.80 \cdot 10^{1}$	$2.33 \cdot 10^{-2}$	$1.44 \cdot 10^{-2}$	$3.01 \cdot 10^{-3}$	$8.14 \cdot 10^{-5}$	$1.76 \cdot 10^{-5}$
FRS	$2.03 \cdot 10^{-5}$	$3.45 \cdot 10^{-5}$	$6.16 \cdot 10^{-6}$	$5.86 \cdot 10^{-7}$	$2.70 \cdot 10^{-6}$	3.13	1.11	$2.49 \cdot 10^{2}$	$2.72 \cdot 10^{3}$	$8.45 \cdot 10^{1}$	0.02	0.65	0.15	$3.45 \cdot 10^{-4}$	$2.19 \cdot 10^{-5}$

The eco-efficiency graphs on the most representative impact categories, considering the minimum selling price of resveratrol versus the environmental loads (**Figure 32**), the production costs against the impact to the environment (**Figure 34**) and the production capacity (**Figure 33**) in relation with the environmental impacts. The graphs are divided into four main quadrants, constructed considering the average values of each variable included in the graph. The eco-efficient scenario is represented with a green background, the non-eco-efficient alternative is represented with a red background and the scenario with an intermediate position between being or not eco-efficient is denoted with a yellow background. It is worth mentioning that the most representative impact categories have been selected for the analysis, since the others have a similar behavior.

Evaluating the eco-efficiency index relating the MSP and the environmental loads (**Figure 32**), the results are potentially adequate for two scenarios, both for the base case and for the optimized ones for the S01-VP and S03-GM valorization schemes, with the optimized one obtaining the best scores. In the case of the S04-ER scenario, also promising results are obtained given the fact that, for the base case, the index obtained is in an intermediate position (yellow region), while when assessing the optimized scenario its position is moved to the eco-efficient one. However, for all the impact categories under evaluation the development of the S05-CW alternative does not attain good results. For the base case scenario, a non-eco-efficient alternative is obtained, given the high associated environmental loads achieved per functional unit, mainly due to the low production rate capacity of the process on resveratrol production. However, it is worth mentioning that, when opting for the optimized scenario, in some impact categories an intermediate position between eco-efficient and non-eco-efficient categorization is reached, specifically on GW, TA and FRS impact categories. These results make sense as these are some of the categories in which the greatest environmental reductions are achieved when evaluating an optimized scenario. On the other hand, when comparing the two most promising scenarios, S01-VP and S03-GM, it is the grape must scenario that presents a MSP, which implies the possibility of having gross benefits and higher economic feasibility of the process, and the lowest associated impact in mostly of the impact categories under assessment, with the exception of TET, for which the vine pruning option is of lower impact.

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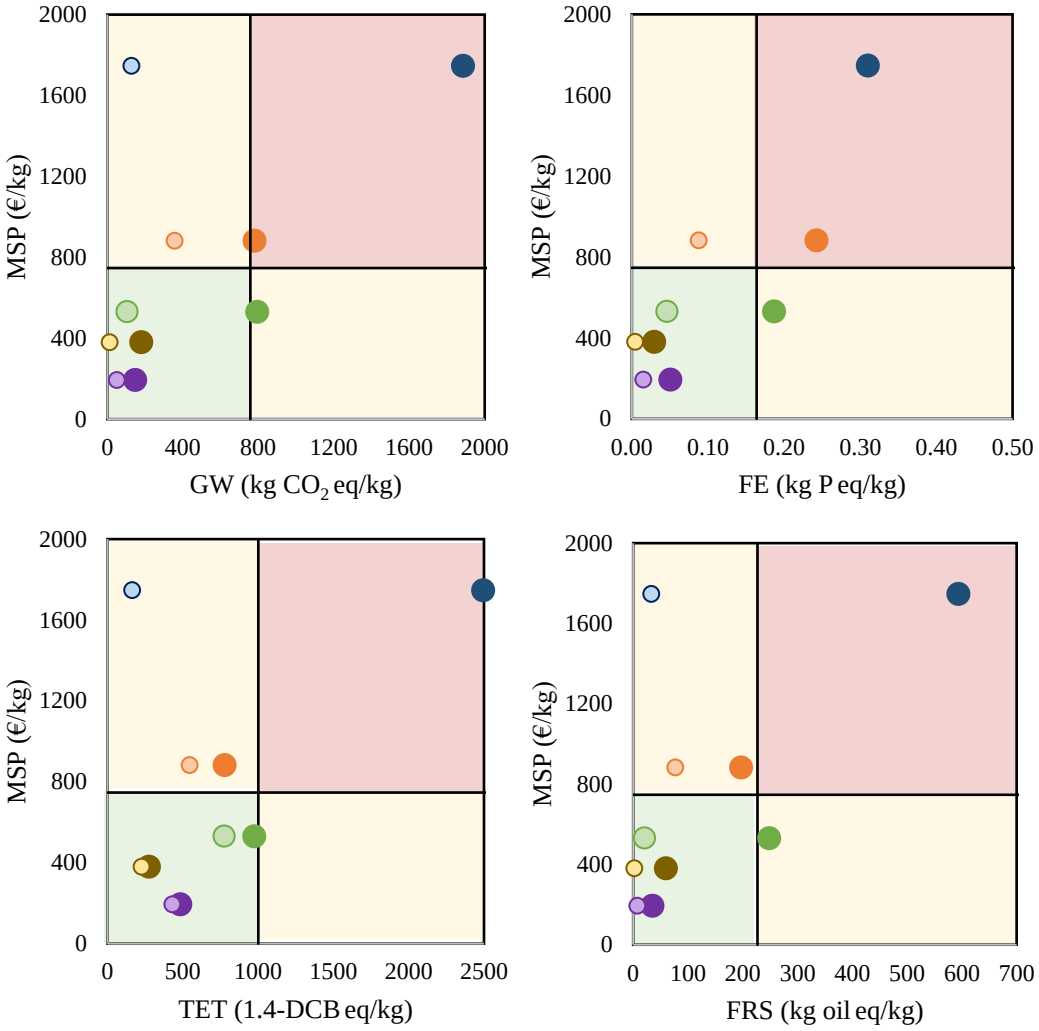

Figure 32. Eco-efficiency analysis considering the index between the minimum selling price of the biotechnological production scheme and the environmental loads. Colour code: ● S01- Vine pruning, ● S02- Grape must, ● S03-Wine lees, ● S04-Eucalyptus residues, ● S05-Cheese whey, ● S01- Vine pruning optimized, ● S02- Grape must optimized, ● S03-Wine lees optimized, ● S04-Eucalyptus residues optimized and ● S05-Cheese whey optimized.

The index that represents the relation between the production costs and the related environmental loads is depicted on **Figure 33.** For the assessment of the scores obtained, two main aspects should be taken into account, (1) a more extensive pretreatment for the release of the fermentable sugars available on the structure of the S01-VP and S04-ER, that implies the need of a hydrothermal, enzymatic and chemical hydrolysis stages and (2) the annual operating/production costs are considering utility costs, labor costs, overheads and material costs, mainly, so that, indirectly, the resveratrol production capacity could influence the value obtained. From this consideration, it has been obtained that, as expected, the S03-WL is the one with the lowest eco-efficiency score, being in fact a non-eco-efficient scenario in both GW and FE impact categories. The associated high environmental burdens together with the high production costs are the rationale for the value obtained.

On the contrary, it is worth noting that, by opting for the sensitivity scenario, the one that considers the use of renewable resources for energy needs in this case, significantly improves the index score obtained, since it is placed, for most impact categories, in an

intermediate position between an eco-efficient and a non-eco-efficient scenario (yellow region in the graphs in **Figure 33**).

As for the most promising alternatives, S01-VP seems to be the most eco-efficient, given its ability to produce such a significant amount of resveratrol by batch process and the related production costs, certainly lower compared to those of grape must. It should be noted that the S04-ER scenario is right on the borderline between classification as an eco-efficient scenario and an intermediate position. Therefore, future research should focus on increasing resveratrol production to some extent or reducing the associated production costs through the use of more efficient equipment, more economical and sustainable utilities, and increased plant automation to reduce labor costs.

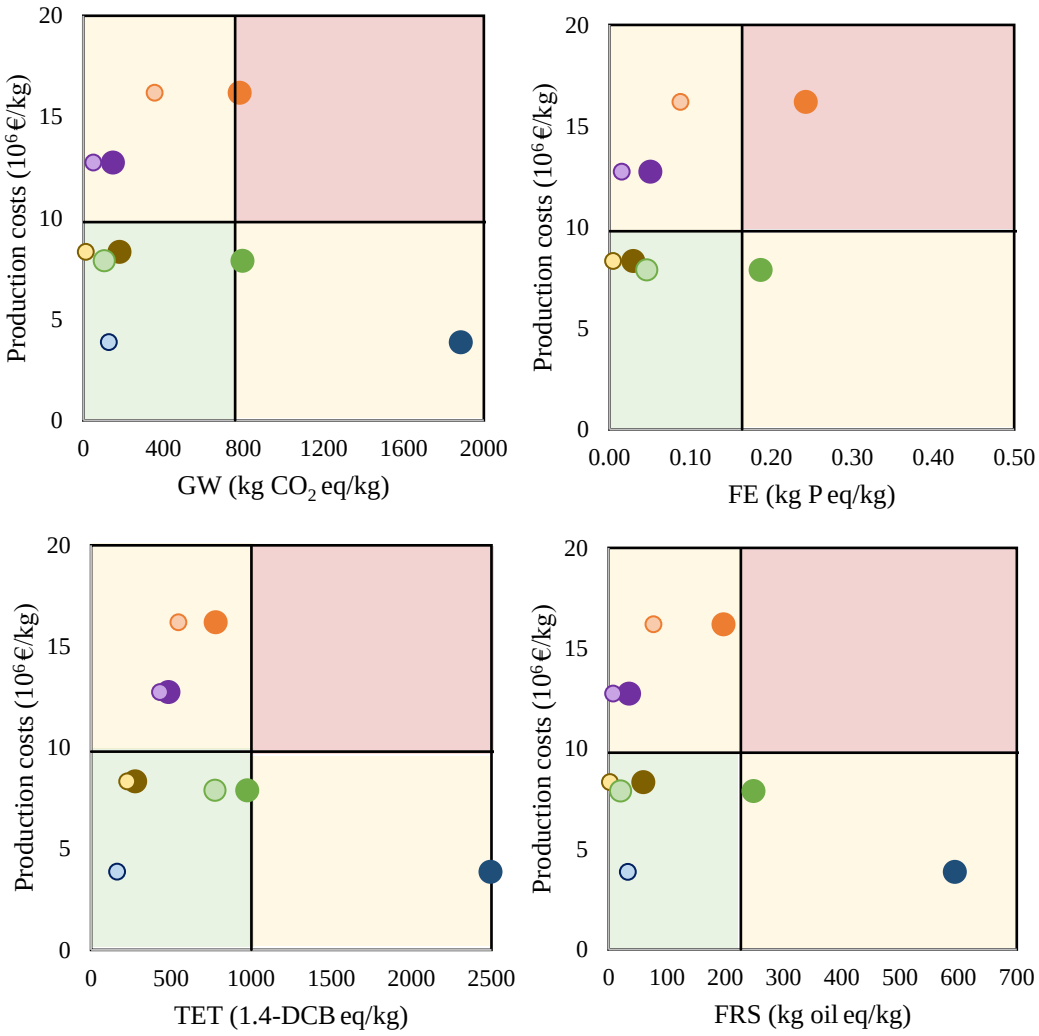

Figure 33. Eco-efficiency analysis considering the index between the production costs of and the environmental loads. Colour code: S01- Vine pruning, S02- Grape must, S03-Wine lees, S04-Eucalyptus residues, S05-Cheese whey, S01- Vine pruning optimized, S02- Grape must optimized, S03-Wine lees optimized, S04-Eucalyptus residues optimized and S05-Cheese whey optimized.

Lastly, the production capacity of the alternatives has been evaluated (**Figure 34**). As expected, according to the modelling values presented in previous sections of this chapter, the S01-VP and S02-GM alternatives are the most eco-efficient, since, per unit

of raw material processed, are the ones capable of generating the highest amount of resveratrol, thus for the S04-ER also promising results are obtained since it is almost encountered in the eco-efficient region for the base case scenario, and achieving it when the sensitivity alternative is analyzed.

As was the case in the previous scenarios of the eco-efficiency index, both S03-WL and S05-CW scenarios are placed in the non-eco-efficient region, given the low resveratrol production capacity compared to the other scenarios, with the exception of the TET and FRS impact categories, for which the S03-WL scenario is located in the intermediate region. On the other hand, it is worth mentioning that, even for the sensitivity scenarios proposed for the aforementioned worst alternatives, not an eco-efficient categorization is obtained. In order to improve the values and to enhance the valorization of those residual streams for the production of resveratrol, further efforts should be placed on the increase of the production capacity, and also on the reduction of the associated environmental loads, which are significantly higher to that of the other alternatives, being the optimization and renewability of energy requirements the actions more adequate to be implemented and improved.

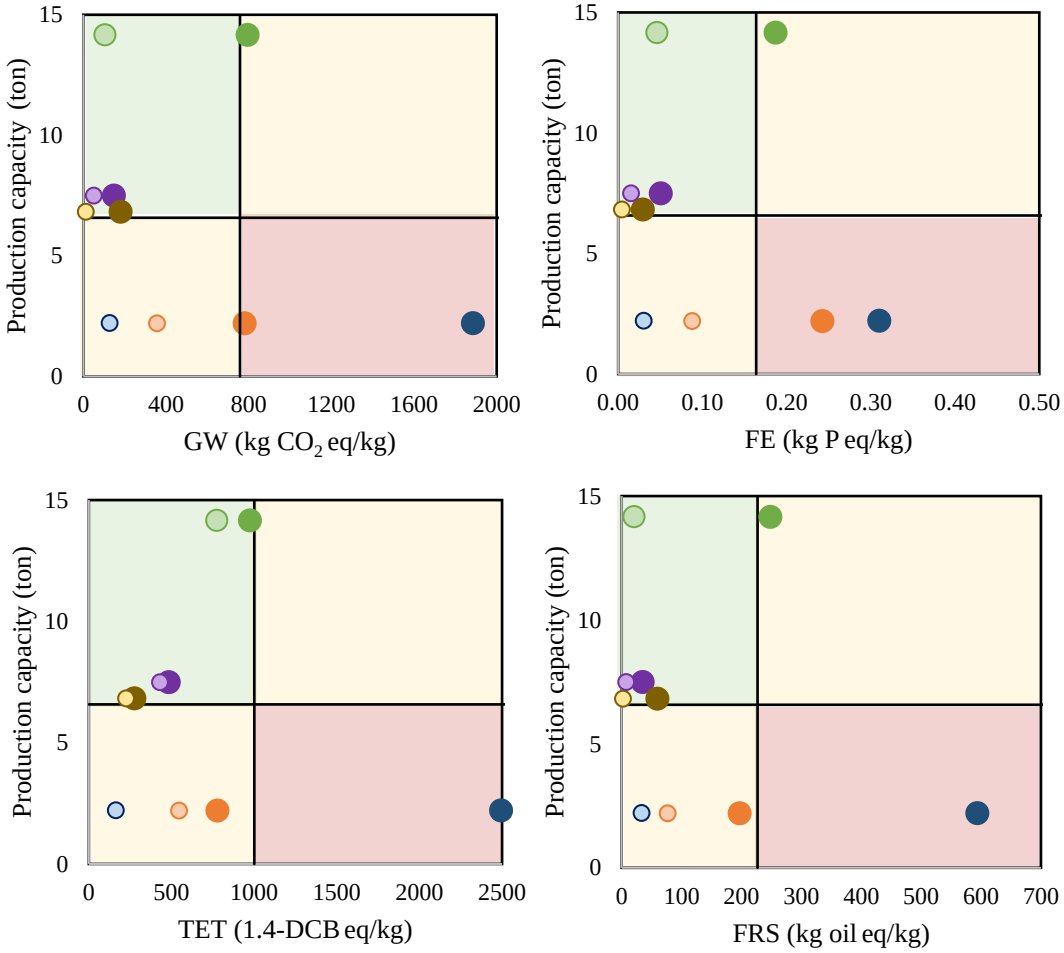

Figure 34. Eco-efficiency analysis for the index production capacity against environmental loads. Colour code: ● S01- Vine pruning, ● S02- Grape must, ● S03-Wine lees, ● S04-Eucalyptus residues, ● S05-Cheese whey, ● S01- Vine pruning optimized, ● S02- Grape must optimized, ● S03-Wine lees optimized, ● S04-Eucalyptus residues optimized and ● S05-Cheese whey optimized.

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13.7 Main outcomes achieved

This chapter has been based on the development of five scenarios of the biotechnological production of resveratrol by a novel engineered yeast strain using five renewable feedstocks related to the food and forestry sectors. The modeling of the process, as well as the analysis of the environmental and techno-economic perspectives, helped to evaluate the feasibility of the scenarios from the technological, economic and environmental approaches within an early stage of development. Taking into account the results obtained, it was possible to conclude that both grape must from vine pruning and eucalyptus residues are feasible substrates for resveratrol bioproduction. However, for the case of wine lees and cheese whey valorization, it is considered that significant improvements are needed to make them more cost-effective and less harmful to the environment, so an alternative valorization process should be considered to promote a more beneficial and sustainable process scheme. But even so, it has been shown that all scenarios are viable in economic terms, since the minimum selling price obtained for the products is lower than the real average market price. However, the energy requirements are the hot spots in the environmental profiles of all the proposed alternatives. Future research should encourage the use of renewable energy sources and also the improvement of process efficiency and performance.

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SECTION VII

General findings and conclusions

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OUTLINE

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Detailed outcomes from the thesis

The environmental impact of fossil fuels, as well as the reduction of their availability, and the huge amount of agricultural, forestry and industrial waste produced annually to meet the demands of the population, lead to the need to develop new production models that promote the use of these waste flows and bet on bio-based models that are committed to the pursuit of sustainability and circularity in production. It is in this approach where this thesis has been framed, which has been built with the challenge of evaluating new biorefinery and biotechnology production schemes to obtain a range of bio-based products, from formaldehyde-free bioadhesives, to antioxidants, antimicrobials and active biofilms for food preservation, with a high market potential.

However, when scenarios have been developed, one of the main challenges for their evaluation under the perspective of their associated environmental impact, as well as their economic feasibility or their framing within what is considered eco-efficient, has been the lack of data availability. The fact that most of these new production schemes are developed at laboratory level, or at most, at pilot level, has implied the need to scale up the processes to a productive capacity analogous to that of traditional production schemes, in order to be able to evaluate their real potential. However, this challenge has been resolved through the use of the SuperPro Designer tool, which although it presents a higher degree of error than would be obtained if real large-scale production data were available, it allows to provide a close and certainly accurate view of the potential of the biological process alternative towards a mass production model.

In order to solve one of the main concerns of the wood-based panel industry, i.e., the reduction or avoidance of formaldehyde in adhesives, given its potential harm to human health, it was decided to use residues from pulp manufacturing, both Kraft lignin and Organosolv, as well as residues from agricultural and forestry activities, such as soybeans, starch or tannins. The main weakness detected in the use of lignin was the need for its activation or functionalization in order to be used as raw material for the bio-adhesive formulation. The most common process is glyoxalation, although the environmental impact of this pre-treatment stage is very significant, given the energy requirements, specifically electricity, since it was found that its impact on the profile exceeds 80% of the overall effect.

However, given the potential characteristics of lignin to be used in the production of bio-adhesives, it was considered to use a different type of functionalization, using methylation with dimethyl carbonate, which resulted in a significant reduction of environmental damage and, therefore, becoming a more viable alternative from the point of view of environmental sustainability.

Similarly, for the use of tannins, a pre-treatment stage was also necessary for their activation, in this case based on obtaining condensed tannins, but, unlike what happened with lignin, the functionalization of this raw material does not have such a high impact on the environmental profile obtained, only around 20-30% compared to the 80% corresponding to the activation of lignin, thus making this residual raw material a more attractive resource from the environmental point of view, which has also been demonstrated when comparing the alternatives of tannin bio-adhesives with respect to synthetic resins, reaching similar or even lower values than the latter.

In addition to assessing raw materials derived from wood resources, it has also been opted to evaluate the potential of proposing bioadhesives scenarios using residual resources from the agri-food industry, such as soybean and starch. At a certain point, there could be some confrontation over the use of these resources since they can be used for animal feed or even for diet supplements, as in the case of soy protein, although it is

important to mention that it was considered to use residues, i.e., unusable parts and, therefore, not suitable for human or animal consumption, a fact that should not be an impediment to their use. Having stated this, it has been observed that the adhesion properties provided by these bioadhesive alternatives are adequate and analogous to those of synthetic resins, although, in order to obtain these good thermogravimetric properties it is necessary to add certain crosslinking agents and other promoters of suitable properties, such as the use of a waterborne polyurethane to improve both the moisture content of the adhesive and its waterproofing, which implies a certain impact on the environmental profile obtained, and sometimes even the main one.

As for the use of starch, as for lignin and tannins, a pre-treatment step is also required, certainly impacting some of the impact categories selected for the environmental assessment, which may consist of an oxidation or hydrolysis of the molecular structure of the starch to increase its active centres and thus favour a correct cross-linking with the other constituents of the bioadhesive, as well as to increase its mechanical adhesion properties. Among the two activation alternatives, hydrolysis is the one that gives rise to a greater environmental contribution, where an implication of more than 70% was observed in the impact categories associated with ecotoxicity and toxicities with influence on human health.

Thus, as a final statement about these two raw materials of agri-food origin, it could be concluded that, although some impact on the environment has been noticed, it has been observed that, in general, both soy and starch bio-adhesive alternatives present lower environmental damage values compared to traditional formaldehyde-based resins, which really implies a high potential of these resources to be considered as alternatives for the partial substitution of synthetic resins.

Moving on from bio-adhesives, this thesis has also provided alternative scenarios for the production of antimicrobials, bioactive compounds with excellent properties demonstrated to be used as natural preservatives, as is the case of nisin. It should be noted that nisin has already been recognized as a GRAS compound, however, its common production route employs synthetic fermentation media, which implies higher associated production costs that reduce the feasibility and potential for the penetration of this bio-based active compound into the market value chain. To this end, this thesis has proposed alternative scenarios in which the use of synthetic media is avoided, whereby the carbon source used is from waste resources, in particular sugar beet pulp, corn stover, cheese whey and wheat straw, such as agri-food based, and eucalyptus and olive pruning residues from agricultural and forestry activities.

To verify the suitability of these side streams for the biotechnological production of nisin, it has been necessary to scale up the process, together with the development of the LCA methodology, techno-economic evaluations, as well as eco-efficiency analyses, to reach a final overall conclusion on their potentiality. The modelling has provided the production capacity of each of the alternatives, being aware that it depends, firstly, on the amount of sugars available, secondly, on the amount of lignocellulosic material in the structure, since the higher the amount, the lower the release of fermentable sugars, and, thirdly, on the number of stages and equipment required for each process scheme.

Both sugar beet pulp, corn stover, eucalyptus residues, olive pruning and wheat straw need intense pretreatment process, given the requirement of cleaving the polysaccharides' structure to enable the release of the fermentable sugars, i.e., autohydrolysis, enzymatic and acid post-hydrolysis. These intense pretreatment implies that these stages are the ones with the highest environmental loads among all the stages of the process, being the energy requirements the main contributors and, in the case of the corn stover alternative, also an

important contribution of the enzymes required for the enzymatic section has also been advertised.

On the contrary, for cheese whey, a simpler pre-treatment is developed, consisting only of a first heat treatment and a second centrifugation step for the release of the protein content, since its presence influences the fermentation yield. However, given the lower nisin production capacity compared to the other scenarios, this alternative is not considered the most promising, sugar beet pulp being in this case the best alternative. The justification for this statement is based not only on the environmental results, but also on the techno-economic ones, since it has been categorized as a profitable and eco-efficient scenario, which is not the case with corn stover valorization, since it does not reach an economic profitability score, nor is it eco-efficient. In addition, olive pruning, eucalyptus residues and cheese whey also appear to be appropriate resources for nisin production, given the values obtained when performing the techno-economic and environmental evaluations, but further improvement is needed to decrease the energy requirements of these alternatives in order to improve their sustainability potential, for which advocating their optimization and the use of renewable resources for their production could be considered key factors.

One step forward for an even increased circular model in the production of this bioactive compound relies on the recovery of the lactic acid co-produced in the fermentation stage. Given that nisin could be used as food preservative and lactic acid could be polymerized to obtain a biofilm, polylactic acid, this approach has been also assessed in the thesis, thus providing a bioactive film for food preservation. In order to assess, from an early stage of design, its suitability, a multicriteria roadmap has also been created, considering both technical, sustainable and circular indicators. Its approximate evaluation has shown that the potentiality of this bioactive film is high, given its bio-based nature, degradability capacity, economic feasibility, and expected social acceptance.

In this case, wheat straw has been selected as the most suitable resource, mainly because of its availability and its potential for the release of fermentable sugars, and also because it has been the one for which the lowest environmental load per kg of nisin produced has been obtained compared to the waste streams mentioned above. The environmental scores have shown that, although the pre-treatment section has a significant burden on the overall environmental profile of the process scheme, it is in line, or even lower, compared to that of the later stage, where purification of both nisin and lactic acid takes place for further processing. While in the case of the last stage, in which lactic acid is polymerized, reduced environmental loads are obtained, making this stage the least harmful to the environment.

To this end, it has been demonstrated the effectiveness of further valorization of the co-produced lactic acid. On the other hand, it should be mentioned that, as previously mentioned, the electricity and steam requirements are the ones with the highest contribution in all the process stages, thus reinforcing the need to optimize its use and the promotion of the use of renewable energies. But even with this bottleneck on the energy needs, the scenario proposed has been catalogued as potentially sustainable following the Greenness Grid methodology, based on the principles of Green Chemistry. Therefore, a scenario with a double benefit has been proposed, as from the valorization of a single bio-based waste stream an active biofilm has been produced that can be applied for food preservation, thus avoiding the use of synthetic preservatives that reduce the nutritional values of the food and modify its organoleptic properties.

In addition to nisin, another focus has been to investigate the potential for the extraction and production of antioxidants from agro-industrial and forestry waste

resources. Regarding extraction, the study has been aimed at evaluating the efficiency, yield and benefits that emerging extraction technologies can provide compared to conventional ones, using sugar beet as renewable residual feedstock. Based on the fact that emerging technologies are thought to be more sustainable, given the reduction on the use of chemicals, the diminished extraction time and the decrease on related emissions. However, the lack of optimization of these technologies could be considered as a drawback for its implementation on a large-scale production scheme. This could be the main result when using ultrasound-assisted extraction, because although it is a very fast extraction technique, with acceptable extraction yields, its electricity consumption makes it a very intensive alternative with significant environmental burdens. However, it should be noted that for all the emerging extraction technologies evaluated, electricity and steam are the main contributors to the environmental profile, whereas for conventional technologies, solvent is the main contributor to most of the impact categories evaluated.

On the other hand, in order to give a more detailed evaluation on the potentiality of emerging technologies over the conventional ones, a techno-economic evaluation has also been developed, with which it has been obtained that the lowest antioxidant selling price required and, hence, the more profitable in terms of economy, are the emerging technologies of supercritical and pressurized extraction, mainly given its lower batch time, thus higher production capacity. Besides, the same result has been achieved when both environmental and economic scores were encompassed within the eco-efficiency analysis, for which both aforementioned emerging technologies have achieved an eco-efficient score for mostly of the indexes evaluated.

On the other hand, besides opting for the extraction of antioxidants from renewable resources, as in the previous case, it is also possible to evaluate the production of antioxidants through a fermentative biotechnological process, in which the residual resources are used as a source of fermentable sugars to produce the antioxidant. This investigation was based on the production of resveratrol, an antioxidant with excellent properties and high applicability in the pharmaceutical, food and medical sectors, among others. Both agro-industrial and forestry resources have been used for this purpose, namely wine production residues, cheese whey and eucalyptus residues.

As in the case of nisin, the advantage of using cheese whey lies in the lack of an intense pretreatment stage for its valorization. Although, given its high protein content, its suitability as a source of sugars is not as high, a fact that is demonstrated by its low resveratrol production capacity compared to the other feedstock alternatives. This limited production implies a greater environmental impact per kg of resveratrol obtained, as well as a low economic profitability given the inability to generate sufficient profits, thus converting it into a non-eco-efficient process alternative. However, the use of this resource for protein recovery could be considered as a suitable scenario, since its high protein content, as well as its ease of separation, mainly based on ultrafiltration stages, turn this alternative into a potential one, both from an environmental and economic point of view.

A similar conclusion could be reached when analyzing the potential of wine lees, although the fermentative medium is also capable of digesting its ethanol content, the low productive efficiency results in a poorly suitable alternative from the point of view of environmental and techno-economic feasibility, despite being a residual raw material that does not require intensive pre-treatment. In view of the results obtained, it could be concluded that opting for the valorization of this waste flow towards the production of biofuels seems to be a more viable option, or at least, more cost-effective compared to its use for the production of resveratrol.

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Concerning the remaining alternatives, the productive capacity is analogous, with the valorization of olive pruning residues yielding the highest amount of resveratrol per batch time, followed by the grape must scenario. Between these two alternatives, the most significant difference lies in the pretreatment stage, since, while grape must can be used directly, pruning residues require an intense pretreatment for the release of sugars, analogous to that presented for the valorization of eucalyptus residues to obtain nisin. This fact has implied that the environmental impacts of pruning residues valorization are higher than those of the grape must, mainly due to the energy requirements, as well as the costs associated with the process, which are almost twice as high. Therefore, it can be concluded that this pretreatment stage is in fact a bottleneck in the attainment of environmental and economic sustainability and, therefore, is where efforts should be focused to minimize its potential impact. Consequently, and with the support of the results obtained by applying the eco-efficiency analysis, it can be concluded that the valorization scheme using grape must is the most promising resveratrol production scenario for both environmental and economic concerns.

As a concluding argument, it should be emphasized that throughout this doctoral thesis diverse evaluation methodologies have been used, the main one being Life Cycle Assessment (LCA), but other alternatives have also been proposed to deepen the analysis of the proposed bio-based scenarios. The most innovative is perhaps that of Planetary Boundaries, which goes one step further than LCA, taking into account the impact values at a global level and considering the limits imposed by the Sustainable Development Goals. The Greenness Grid method has also been used, in which more emphasis is placed on safety, derivatives production, effectiveness in the use of carbon compounds, as well as on risk factors, aspects on which the LCA methodology is not as focused. On the other hand, it has been found that it is important to combine environmental and techno-economic results in order to select which alternative has the greatest marketability, for which the eco-efficiency analysis has been used. Although analogies have been noted between the results provided by the different methodologies, it is believed necessary to consider this diversity of methods to be able to demonstrate in greater detail the adequacy of the processes under study. Furthermore, in the development of the doctoral thesis, a lack of research reports integrating sustainability and circularity aspects has also been noted, and in this aspect, a multi-criteria map has been provided in which indicators from these two areas are incorporated to determine the suitability of a product design prototype.

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Research gaps and future perspectives

By the discussion of the main outcomes and conclusions of this thesis dissertation, some research gaps and future recommendations has been identified. On the one hand, regarding the scalability of bio-based process, the unavailability of industrial-scale production data leads to a certain degree of inaccuracy, since it implies the performance of a large-scale modeling of the process, for which process data (such as yields, doses of chemicals used, process times, etc.) similar to those of the laboratory are used, which are not always optimized to promote more efficient processes This really implies a high contribution both on the environmental profile obtained and on techno-economic aspects. For this reason, the development of pilot scale production models may be the most appropriate strategy to promote the integration of biorefinery and biotechnology production models on an industrial scale, as well as for the evaluation of their degree of sustainability and economic effectiveness in a more realistic manner. In addition, another aspect to improve, from the point of view of modeling software, is that it should be more oriented towards biological processes, since the modeling of biorefineries or biotechnological processes under the approach of a chemical production model may imply certain disadvantages in terms of economic viability.

With respect to the environmental evaluation, the results provided by the Life Cycle Assessment methodology has certain limitations when it comes to assessing how the process under analysis affects the quality of the environment from a more global, planetary level. It could be said that LCA provides a snapshot of how the process scenario contributes to environmental quality within a specific radius of impact, for example, on a regional scale. This fact is already observable when selecting the life cycle inventory, for example for the energy aspect, where the data basis for electricity requirements are those for a given region. Therefore, opting for additional methodologies that not only provide a "local" but also a more "global" view would be fundamental, as developed in Chapter 7 of this thesis. The evaluation of the degree of adequacy through the calculation of planetary boundaries is still a model of evaluation not widely present in the literature, given the complexity of its calculation and the need to deal with extensive databases by sector. That is why in the future it should be committed to provide a tool, as is the case of SimaPro, the characteristic of the LCA methodology, capable of evaluating the scenarios from a planetary boundary's perspective. This approach would not only provide the degree of adequacy of a scenario from the point of view of the established global thresholds, but would also allow to determine in which location it would be more suitable to implement a biorefinery or industrial symbiosis model, since it would take into account factors such as GHG emissions by sector and country, community demand, as well as economic factors of final capital expenditure or gross value added of the industrial sector, among others.

In line with the previous statement, the use of alternative methodologies to LCA throughout the thesis has provided a more extensive view of the degree of appropriateness of the scenarios. The development of those methodologies has allowed to identify that, for example, the Greenness Grid methodology is sometimes not able to really show the suitability of each of its scenarios, or to establish a comparison between them, especially when the only thing that changes in the process is the type of raw material used or some characteristic stages. For this reason, although it is a useful methodology for measuring the degree of sustainability of a scenario under evaluation, it should be borne in mind that the parameters it measures are not analogous to those of the LCA methodology or the eco-efficiency evaluation, but rather it measures this potential from the point of view of the principles of the Green Chemistry. Therefore, emphasis is placed on the need to

evaluate the scenarios from different perspectives, using various methodologies, in order to effectively and accurately identify their potential, since using only one type of methodology can lead to mistaken hypotheses.

More focused on the results achieved, it has been observed that the contribution of energy consumption is significant for most of the cases, which has led to perform sensitivity analyses to evaluate how its modification implies an integral improvement on the profile obtained. Although the optimization of energy use implies a substantial impact reduction, the use of renewable energies improves the environmental profile even more. This is why future biorefinery and biotechnology models should not only focus on using bio-based raw materials or fermentation models with bacterial populations to avoid the use of chemicals, but also should advocate for totally renewable energy sources, or at least a high percentage of them, since this would imply a much lower degree of environmental impact and economic feasibility.

As a general conclusion, it could be stated that throughout the development of the thesis, the importance of using different approaches when evaluating the scenarios has been demonstrated. As sometimes a biorefinery model may be adequate from the point of view of environmental sustainability, but on the other hand, it may not provide sufficient production productivity to be categorized as economically viable. A positive evaluation of both items is fundamental for the implementation of new bio-based models, but so is social acceptance, i.e. social sustainability, the third pillar of sustainable development. While it would be interesting to have implemented this study in the scenarios proposed in this thesis, the impossibility of accessing data from the sector, as well as the lack of a detailed and updated methodology guide has not made it possible. The rationale behind this is basically based on the fact that those lacks imply a high degree of imprecision, given the need to make assumptions or simply not being able to consider certain important items in the social sphere due to the impossibility to access to data on them. Therefore, in the future, efforts should be made to develop a social impact assessment methodology with a similar degree of accuracy to that of LCA, as well as to provide accurate databases with updated information on the sector and, if possible, also on the type of product available on the market. In this way, the three pillars of sustainability would be integrated in the studies of early designs of biorefinery and biotechnological production models, which would imply a further step in the preliminary and future evaluation of their degree of suitability.

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General outcome of the thesis

This PhD thesis has proposed a series of bio-based scenarios with the aim of proposing new production models that are more sustainable and that enhance the use of resources in an integral manner, thus promoting the circular economy of the supply chain. It is important to highlight that the term "bio" is not always synonymous of "sustainable", since it implies the development of processes with a much lower degree of optimization when compared to more conventional production models based on fossil resources. This fact has been demonstrated during most of the chapters of the thesis, where it has been found that in various environmental profiles, energy consumption is the main contributor to the associated impacts, given the lack of energy optimization and the low degree of development.

On the other hand, it is important to mention that these studies have been developed through large scale modeling using laboratory data, not pilot scale, which also implies that the degree of improvement and optimization is high, and therefore also its associated impacts, as well as its economic feasibility. Although, even though this series of drawbacks may reduce to some extent the integration of bio-based processes and products in the market, it has been observed that most of the scenarios proposed throughout this thesis are feasible from the economic point of view, a fact demonstrated through the performance of techno-economic analyses, as well as adequate from the environmental perspective, having in some cases a lower associated impact compared to conventional production models.

Therefore, the results of this thesis dissertation could be considered as a further step in the integration of bio-based production processes in the market chain, which encourage the integral use of resources, the recovery of waste and the use of more environmentally friendly technologies. It is expected that the results shown will serve as a basis for the development of new biorefinery and biotechnology process alternatives and for the promotion of industrial symbiosis, which could be an efficient practice to reduce the amount of wastes being generated in the industrial and agricultural sector.

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ANNEX I: Publications

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Published articles used in this thesis: rights, contributions and quality indicators.

Process modelling and environmental assessment on the valorization of lignocellulosic waste to antimicrobials

Arias, A., Feijoo, G., Moreira, M.T.

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***Food and Bioproducts Processing*.** ISSN: 0960-3085, volume 137, Issue 2023, pages 113-123, 2022. DOI: 10.1016/j.fbp.2022.11.008

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The journal Food and Bioproducts Processing currently presents an impact factor of 5.105 (2021 Journal Citation Reports), a Cited Score Index of 7.2 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 2 (Q2) in "Biotechnology & applied microbiology" (45/159), in "Engineering, chemical" (38/143) and in "Food science & technology" (38/144).

At the year of publication (2022) the scores are the same of the aforementioned.

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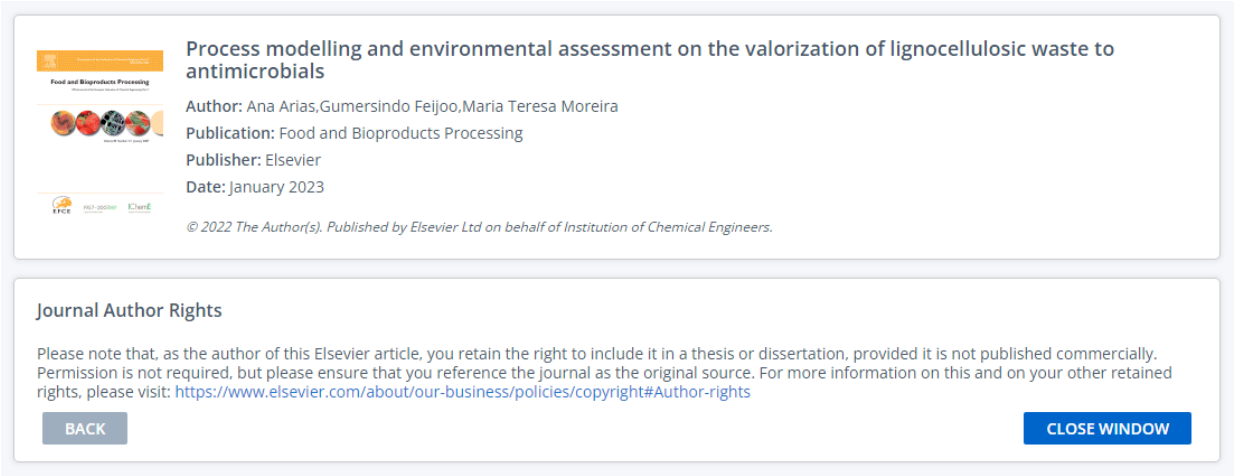

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New Environmental Approach Based on a Combination of Planetary Boundaries and Life Cycle Assessment in the Wood-Based Bioadhesive Market

Arias, A., Feijoo, G., Moreira, M.T.

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***ACS Sustainable Chemistry & Engineering*.** ISSN: 2168-0485, Volume 10, Issue 34, pages 11257-11272, 2022. DOI: 10.1021/acssuschemeng.2c03058

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The journal ACS Sustainable Chemistry & Engineering currently presents an impact factor of 9.224 (2021 Journal Citation Reports), a Cited Score Index of 14.5 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 1 (Q1) in "Chemistry, multidisciplinary" (29/179), in "Engineering, chemical" (13/143) and in "Green and sustainable science & technology" (10/47).

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Assessing of the most appropriate biotechnological strategy on the recovery of antioxidants from beet wastes by applying the life cycle assessment (LCA) methodology

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***Food and Bioproducts Processing*.** ISSN: 0960-3085, volume 135, Issue 2022, pages 178-189, 2022. DOI: 10.1016/j.fbp.2022.08.003

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The journal Food and Bioproducts Processing currently presents an impact factor of 5.105 (2021 Journal Citation Reports), a Cited Score Index of 7.2 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 2 (Q2) in "Biotechnology & applied microbiology" (45/159), in "Engineering, chemical" (38/143) and in "Food science & technology" (38/144).

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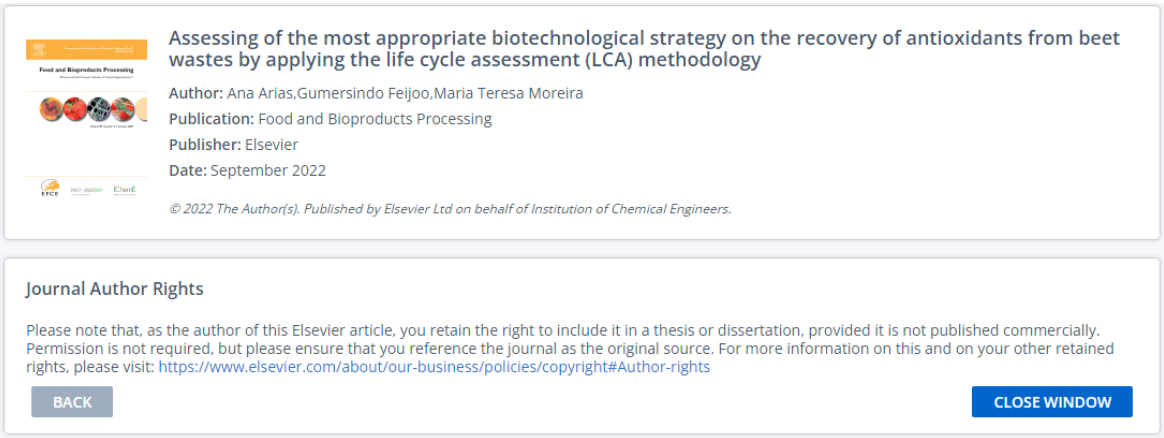

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Technological feasibility and environmental assessment of polylactic acid-nisin-based active packaging

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***Sustainable Materials and Technologies*.** ISSN: 2214-9937, volume 33, Issue 2022, pages e00460, 2022. DOI: 10.1016/j.susmat.2022.e00460

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The journal Sustainable Materials and Technologies currently presents an impact factor of 10.681 (2021 Journal Citation Reports), a Cited Score Index of 9.7 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 1 (Q1) in "Energy & fuels" (17/119), in "Green & sustainable science & technology" (8/47) and in "Materials science, multidisciplinary" (46/345).

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Sustainable non-isocyanate polyurethanes bio-adhesives for engineered wood panels are revealed as promising candidates to move from formaldehyde-based alternatives

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***Journal of Environmental Chemical Engineering*.** ISSN: 2213-2929, Volume 10, Issue 1, 107053, 2022. DOI: 10.1016/j.jece.2021.107053

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The Journal of Environmental Chemical Engineering currently presents an impact factor of 7.968 (2021 Journal Citation Reports), a Cited Score Index of 7.7 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 1 (Q1) in "Engineering, chemical" (20/143) and in "Engineering, environmental" (12/54).

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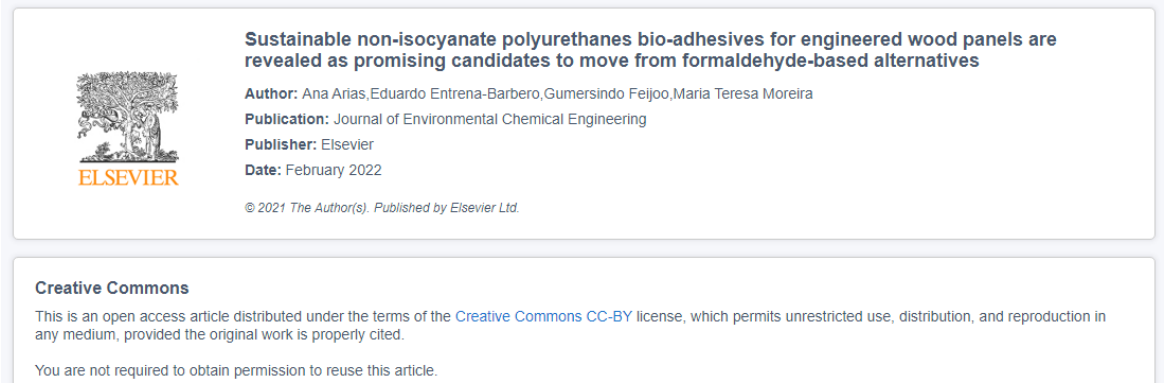

Sustainable non-isocyanate polyurethanes bio-adhesives for engineered wood panels are revealed as promising candidates to move from formaldehyde-based alternatives

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Tannin-based bio-adhesives for the wood panel industry as sustainable alternatives to petrochemical resins

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***Journal of Industrial Ecology*.** ISSN: 1088-1980, Volume 26, Issue 2, pages 627-642, 2022. DOI: 10.1111/jiec.13210

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The Journal of Industrial Ecology currently presents an impact factor of 7.202 (2021 Journal Citation Reports), a Cited Score Index of 12.0 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 1 (Q1) in "Environmental sciences" (49/279) and a quartile 2 (Q2) in "Engineering, environmental" (16/54) and in "Green & sustainable science & technology".

At the year of publication (2021) the scores are the same of the aforementioned.

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Establishing the multi-criteria roadmap and metrics for the evaluation of active films for food packaging

Arias, A., Feijoo, G., Moreira, M.T.

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***Current Research in Green and Sustainable Chemistry*.** ISSN: 2452-2236, Volume 4, Issue 2021, 100160, 2022. DOI: 10.1016/j.crgsc.2021.100160

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

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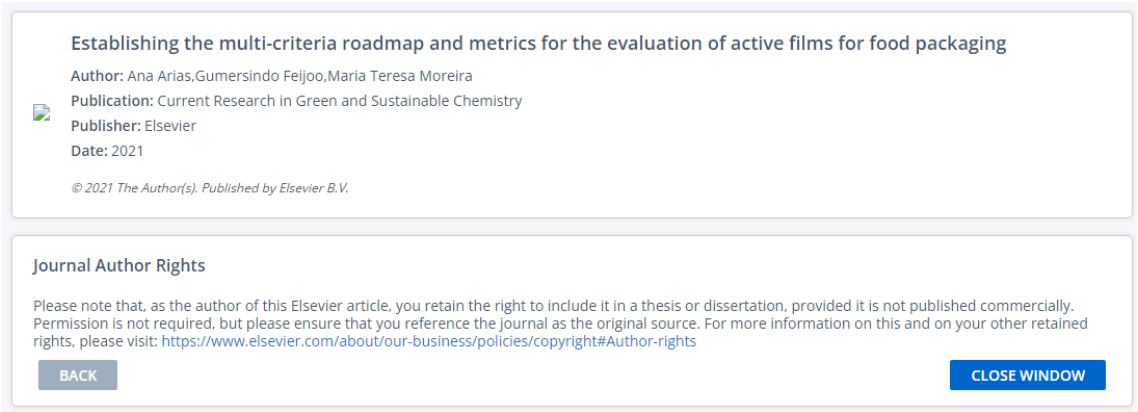

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Evaluation of starch as an environmental-friendly bioresource for the development of wood bioadhesives

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***Molecules*.** ISSN: 1420-3049, Volume 26, 4526, 2021. DOI: 10.3390/molecules26154526

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The journal Molecules currently presents an impact factor of 4.927 (2021 Journal Citation Reports), a Cited Score Index of 5.9 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 2 (Q2) in "Biochemistry & molecular biology" (114/297) and in "Chemistry, multidisciplinary" (65/179).

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Process and environmental simulation in the validation of the biotechnological production of nisin from waste

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***Biochemical Engineering Journal*.** ISSN: 1369-703X, Volume 174, 2021, 108105. DOI: 10.1016/j.bej.2021.108105

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation and writing – original draft of the research article.

Quality indicator

The Biochemical Engineering Journal currently presents an impact factor of 4.446 (2021 Journal Citation Reports), a Cited Score Index of 6.7 (according to Scopus, 04/05/2023) and the next positions in the different categories: quartile 2 (Q2) in "Biochemistry & applied microbiology" (55/159) and in "Engineering, chemical" (49/143).

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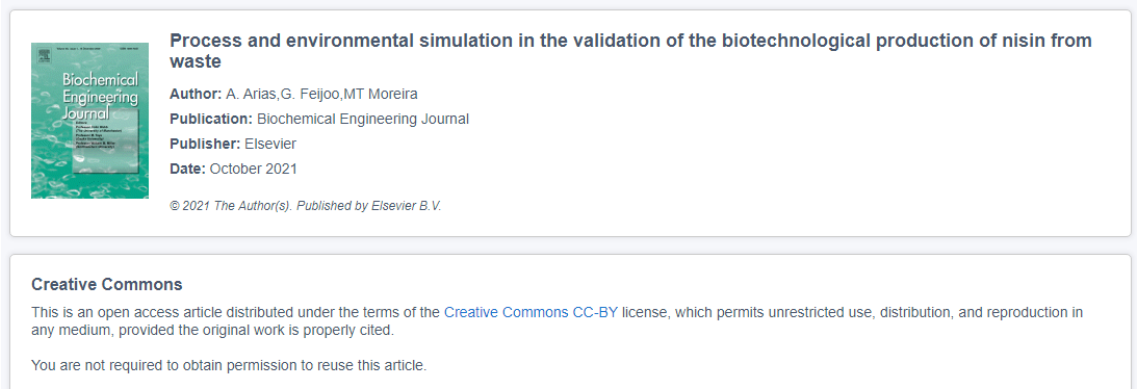

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Environmental benefits of soy-based bio-adhesives as an alternative to formaldehyde-based options

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***Environmental Science and Pollution Research*.** ISSN: 0944-1344, Volume 28, 2021, pages 29781-29794. DOI: 10.1007/s11356-021-12766-4

Specific contribution to the publication

Ana Arias performed the investigation, methodology, writing-original draft preparation and writing-review and editing of the manuscript.

Quality indicator

The Environmental Science and Pollution Research journal currently presents an impact factor of 5.190 (2021 Journal Citation Reports), a Cited Score Index of 6.6 (according to Scopus, 04/05/2023) and the next positions in the category: quartile 2 (Q2) in "Environmental Sciences" (82/279).

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Cradle-to-gate Life Cycle Assessment of bio-adhesives for the wood panel industry. A comparison with petrochemical alternatives

Arias, A., González-García, S., González-Rodríguez, S. Feijoo, G., Moreira, M.T.

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Science of the Total Environment. ISSN: 0048-9697, Volume 738, 2020, 140357. DOI: 10.1016/j.scitotenv.2020.140357

Specific contribution to the publication

Ana Arias performed the methodology of the research article.

Quality indicator

The Science of the Total Environment journal currently presents an impact factor of 10.754 (2021 Journal Citation Reports), a Cited Score Index of 14.1 (according to Scopus, 04/05/2023) and the next positions in the category: quartile 1 (Q1) in "Environmental sciences" (26/279).

At the year of publication (2020) the scores for the impact factor were 7.963, the Cited Score Index of 10.5 and the position in the category of "Environmental sciences" was also a quartile 1 (Q1) (25/274).

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Submitted but not published***: Environmental and techno-economic assessment on the valorization of vine-side streams to produce resveratrol.***

Arias, A.[1], Costa, C.E.[2,3], Moreira, M.T[1], Feijoo, G.[1], Domingues, L[2,3].

[1]CRETUS, Department of Chemical Engineering, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain

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[3]LABBELS - Associate Laboratory, Braga/Guimarães, Portugal

Science of the Total Environment. ISSN: 0048-9697

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation, writing-original draft and writing-review and editing of the research article.

Quality indicator

The Science of the Total Environment journal currently presents an impact factor of 10.754 (2021 Journal Citation Reports), a Cited Score Index of 14.1 (according to Scopus, 04/05/2023) and the next positions in the category: quartile 1 (Q1) in "Environmental sciences" (26/279).

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Submitted but not published***: Process modeling, environmental and economic sustainability of the valorization of whey and eucalyptus residues for resveratrol biosynthesis.***

Arias, A.[1], Costa, C.E.[2,3], Moreira, M.T[1], Feijoo, G.[1], Domingues, L[2,3].

[1]CRETUS, Department of Chemical Engineering, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain

[2] CEB - Center of Biological Engineering, University of Minho, 4710-057 Braga, Portugal

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Waste management. ISSN: 1879-2456

Specific contribution to the publication

Ana Arias performed the methodology, formal analysis, investigation, writing-original draft and writing-review and editing of the research article.

Quality indicator

The Waste Management journal currently presents an impact factor of 8.816 (2021 Journal Citation Reports), a Cited Score Index of 14.1 (according to Scopus, 04/05/2023) and the next positions in the following categories: quartile 1 (Q1) in "Environmental sciences" (36/279) and in "Engineering, environmental" (11/54).

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Total number of research reports published during doctoral studies.

Arias, A., Feijoo, G., Moreira, M. T. (2022). Process modelling and environmental assessment on the valorization of lignocellulosic waste to antimicrobials. *Food and Bioproducts Processing*.

Arias, A., Feijoo, G., Moreira, M. T. (2022). New Environmental Approach Based on a Combination of Planetary Boundaries and Life Cycle Assessment in the Wood-Based Bioadhesive Market. *ACS Sustainable Chemistry & Engineering*, *10*(34), 11257-11272.

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Arias, A., Feijoo, G., Moreira, M. T. (2022). Technological feasibility and environmental assessment of polylactic acid-nisin-based active packaging. *Sustainable Materials and Technologies*, *33*, e00460.

Arias, A., Feijoo, G., Moreira, M. T. (2022). Exploring the potential of antioxidants from fruits and vegetables and strategies for their recovery. *Innovative Food Science & Emerging Technologies*, 102974.

Arias, A., Barreiro, D., Feijoo, G., Moreira, M. T. (2022). Waste biorefinery towards a sustainable biotechnological production of pediocin: Synergy between process simulation and environmental assessment. *Environmental Technology & Innovation*, *26*, 102306.

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Arias, A., Feijoo, G., Moreira, M. T. (2021). Evaluation of starch as an environmental-friendly bioresource for the development of wood bioadhesives. *Molecules*, *26*(15), 4526.

Arias, A., González-Rodríguez, S., Barros, M. V., Salvador, R., de Francisco, A. C., Piekarski, C. M., Moreira, M. T. (2021). Recent developments in bio-based adhesives from renewable natural resources. *Journal of Cleaner Production*, *314*, 127892.

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Arias, A., González-García, S., Feijoo, G., Moreira, M. T. (2021). Environmental benefits of soy-based bio-adhesives as an alternative to formaldehyde-based options. *Environmental Science and Pollution Research*, *28*(23), 29781-29794.

Arias, A., González-García, S., González-Rodríguez, S., Feijoo, G., Moreira, M. T. (2020). Cradle-to-gate Life Cycle Assessment of bio-adhesives for the wood panel industry. A comparison with petrochemical alternatives. *Science of The Total Environment*, *738*, 140357.

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González-Rodríguez, S., Arias, A., Feijoo, G., Moreira, M. T. (2022). Modelling and Environmental Profile Associated with the Valorization of Wheat Straw as Carbon Source in the Biotechnological Production of Manganese Peroxidase. *Sustainability*, *14*(8), 4842.

Santiago, B., Calvo, A. A., Gullon, B., Feijoo, G., Moreira, M. T., Gonzalez-Garcia, S. (2020). Production of flavonol quercetin and fructooligosaccharides from onion (Allium cepa L.) waste: An environmental life cycle approach. *Chemical Engineering Journal*, *392*, 123772.

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Conferences attended.

Arias, A., González-García, S., Feijoo, G., Moreira, M.T. "The environmental viability of bioadhesives for wood panel industry". Oral presentation. IV Research Symposium on Environmental Technologies, 9th September 2020, Santiago de Compostela (Spain).

Arias, A., Feijoo, G., Moreira, M.T. "The bio-technological waste-to-product route as a model of sustainability: design of strategies for green environmental management". Oral presentation. International Conference on Cleaner Production and Sustainability (CPS 2021), 10th September 2021, Philippines (Online).

Arias, A., Feijoo, G., Moreira, M.T. "Techno-economic assessment of the biotechnological co-production of nisin and lactic acid from food industry residues". Oral presentation. V Research Symposium on Environmental Technologies, 23th September 2021, Santiago de Compostela (Spain).

Arias, A., Feijoo, G., Moreira, M.T. "Valorization of agro-industrial residual streams as a strategy for sustainability". Oral presentation. Sustainable Biorefinery Network. University of Basque Country UPV/EHU, 13th December 2021, Basque Country (Online).

Arias, A., Feijoo, G., Moreira, M.T. "Forestry and crop residues to natural antimicrobials. Bridging the gap from a biotechnological and holistic approach". Poster presentation. III Bio Iberoamerica: Ibero-american congress on biotechnology, 7th-9th April 2022, Braga (Portugal).

Feijoo, H., Arias, A., Moreira, M.T. "Closing the loop through the valorization of glycerol as a substrate in the production of hyperthermophilic beta-glucosidase. A life cycle perspective" Oral presentation. 9th International Conference on Sustainable Solid Waste Management, 14th-16th June 2022, Corfu (Greece).

Feijoo, G., Arias, A., Cambeses, C., Estévez, S., Moreira, M.T. "Divulgando la Ingeniería Química a través de los memo-juegos". Poster presentation. VI Congreso de Innovación Docente en Ingeniería Química (CIDIQ), 11th July 2022, Madrid (Spain)

Arias, A., Nika, C.E., Vasilaki, V., Feijoo, G., Moreira, M.T., Katsou, E. "Environmental, economic and circularity assessment of the hydrothermal liquefaction of black liquor under a biorefinery approach" "10th International Conference on Sustainable Solid Waste Management, 21th – 24th June 2023, Chania (Crete, Greece).

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Awards.

1st Best Oral Presentation for the "Techno-economic assessment of the biotechnological co-production of nisin and lactic acid from food industry residues" on the V Research Symposium on Environmental Technologies, on 23th September 2021, Santiago de Compostela (Spain)

Selected as a Subject Editor for the Energy, Ecology and Environment journal, from the editorial Springer.

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ANNEX II: Supplementary figures

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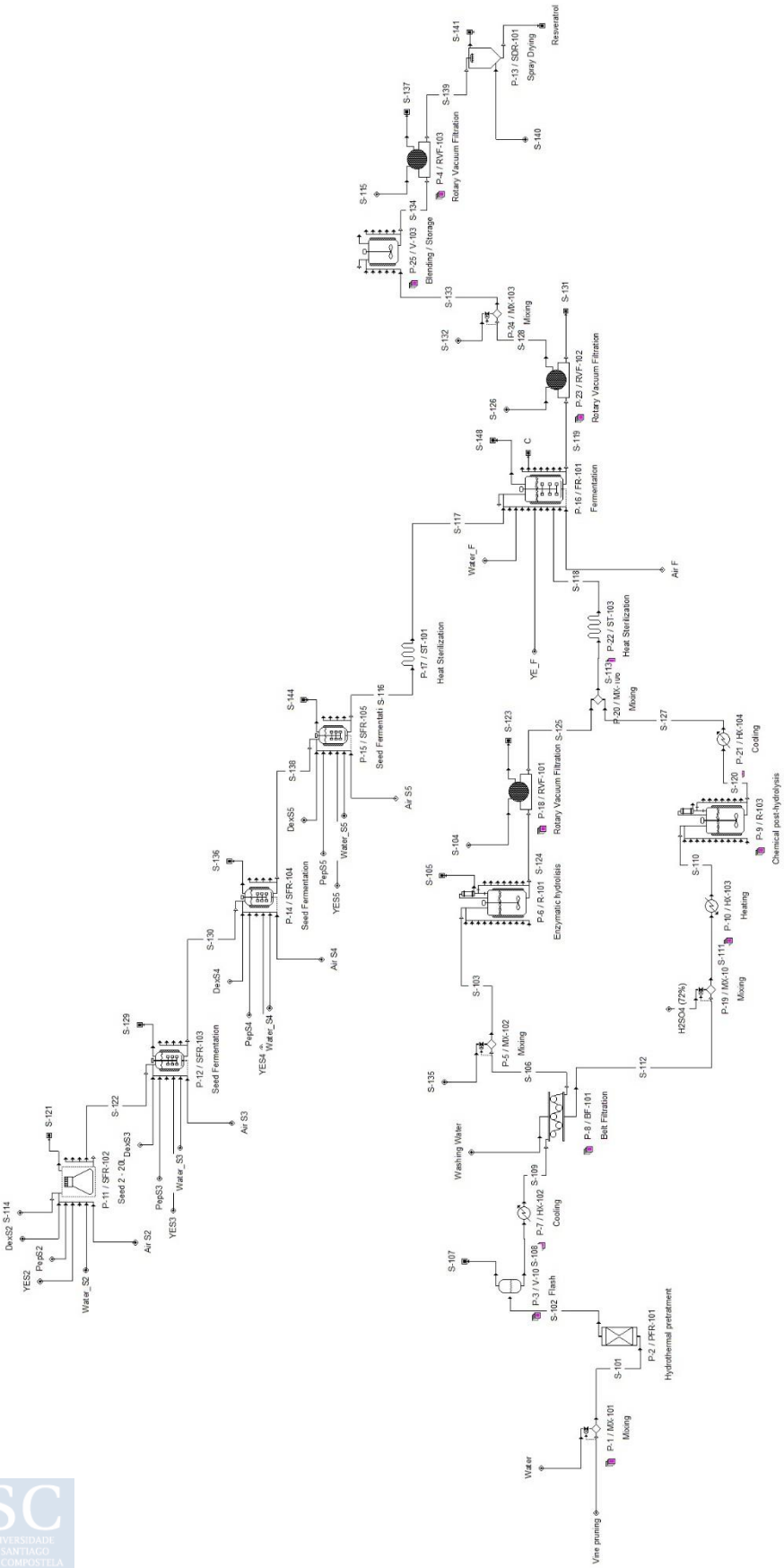

Figure SM2. SuperPro Designer modelling of olive pruning to produce resveratrol.

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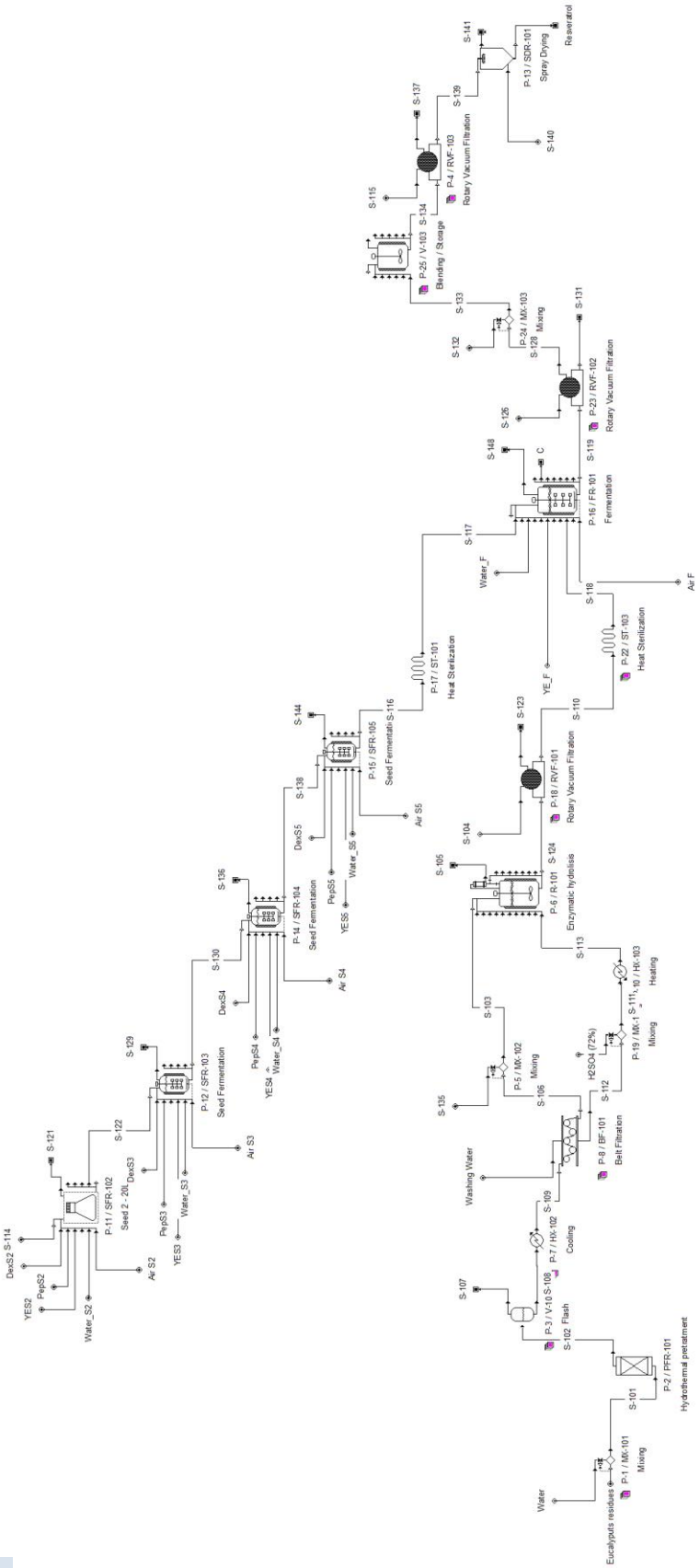

Figure SM2. SuperPro Designer modelling of eucalyptus residues to produce resveratrol.

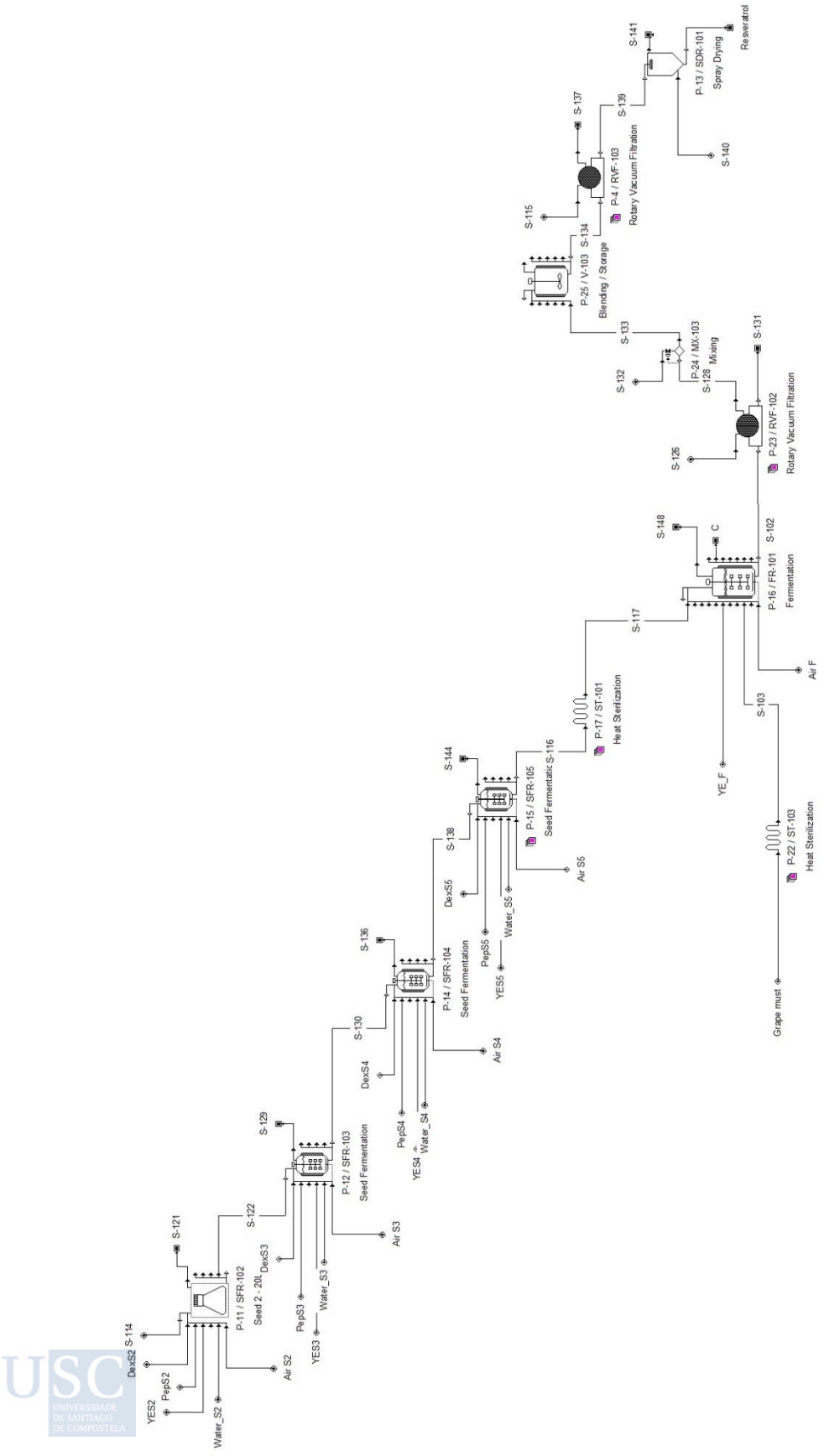

Figure SM3. SuperPro Designer modelling of grape must to produce resveratrol.

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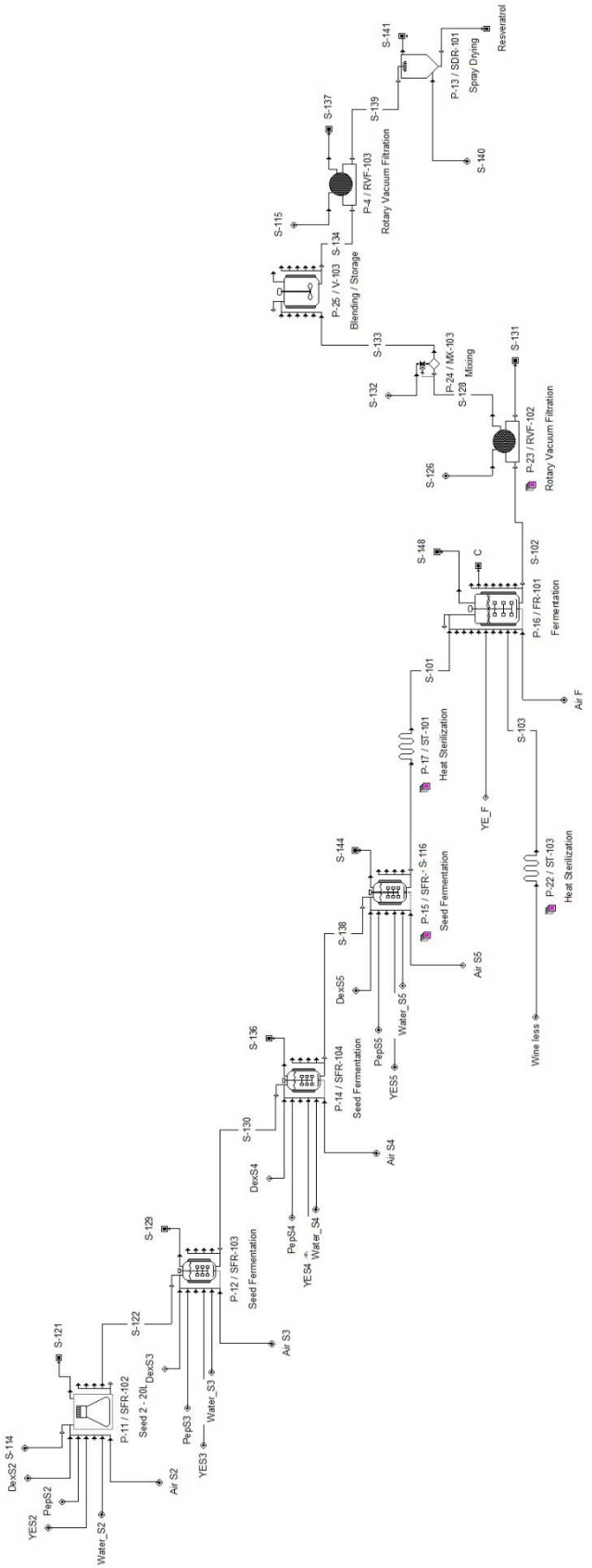

Figure SM4. SuperPro Designer modelling of wine lees to produce resveratrol.

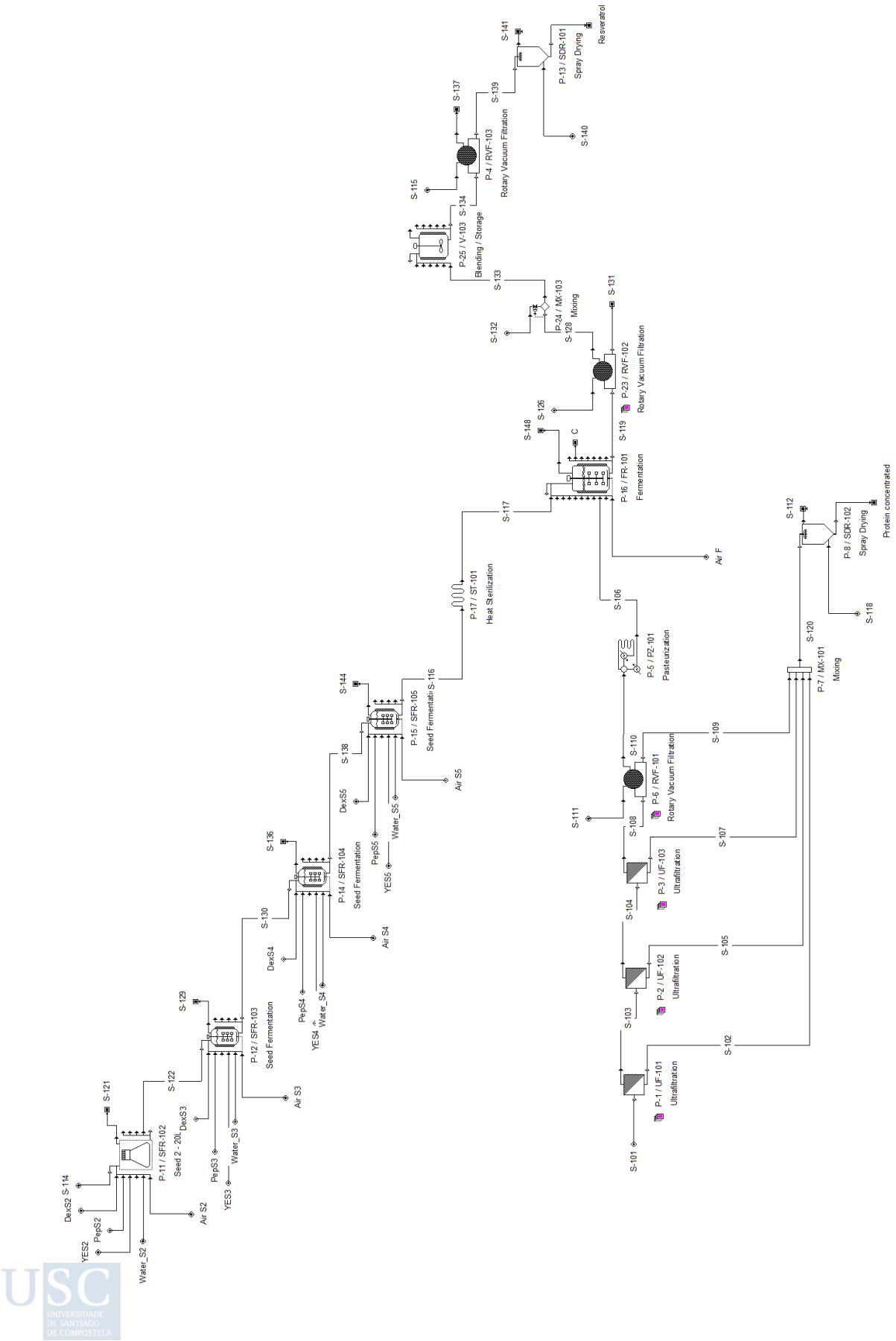

Figure SM5. SuperPro Designer modelling of cheese whey to produce resveratrol.

ANNEX III: Funding

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Funding

I would like to thank the financial support provided by WoodBAdh (PCI2018-092866) co-funded by the ERA-CoBioTech program, NEPTUNUS (EAPA_576/2018), co-funded by the European Regional Development Fund (ERDF) in the framework of INTERREG Atlantic Area, Innovaguas 4 (2022-CP060), an autonomous project funded by the Xunta de Galicia and SPOTLIGHT (PDC2021-121540-I00) a national project funded by the AEI (*Agencia Estatal de Investigación*). I would also like to highlight my involvement in the iFermenter project (790507), funded by the Bio Based Industries Joint Undertaken under the European Union's Horizon 2020 research and innovation program and the Bio Based Industries consortium.

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The increase in the world's population is a challenge for primary, secondary producers and industrial companies to meet the demands of consumers for goods and services. In this context, the search for bio-based resources and with lower associated environmental impacts is a high potential strategy. Forest resources and non-expoitable flows from agri-food sector have become key elements in the search for a sustainable use of resources.

Therefore, this thesis dissertation is framed on the development of biotechnological processes based on the use of waste resources from forestry and the agri-food sector, proposing new production model strategies to obtain high added value products, which are evaluated through sustainability methodologies to asses their main advantages and bottlenecks.