



Boosting the transition to biorefineries in compliance with sustainability and circularity criteria

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ABSTRACT

In the transition towards climate neutrality, biorefinery models are considered promising alternatives to processes based on fossil fuels and non-renewable materials. This consideration is attributed to the reduction of dependence on non-renewable systems, in line with greener and lower impact technological strategies. However, they imply a profound transformation of the production system, as the variable and stochastic nature of certain renewable sources makes it necessary to have various tools to provide flexibility and optimize the system. Their market penetration is currently limited by their level of development and the regulatory and financial support to implement the paradigm shift. Traditional linear production is still more economically viable compared to circular production models, based on efficiency parameters achieved by years of manufacturing experience. To reverse this trend, it is necessary to leverage its benefits through the use of appropriate assessment tools, as these are the ones that could drive the move towards biorefineries. This is the focus of this research report, which reviews various evaluation methodologies and indicators to effectively evaluate bio-based process schemes. Life Cycle Assessment (LCA), Product Environmental Footprint (PEF), Green Chemistry Principles (GCP), certification scheme requirements and Circular Economy Action Plans are reviewed and integrated into a precise assessment framework. To determine their effectiveness, three biorefinery models were evaluated: valorization of apple vinasses, grape must and chickpea peel. Through the combined analysis of bio-based scenarios, it has been possible to identify their benefits, bottlenecks and limitations, and to validate a comprehensive assessment framework that allows an accurate, effective and conscious analysis of bio-based models, promoting their development and market penetration.

1. Introduction: Unlocking sustainability and circularity

The target of sustainability is pursued in all sectors and value chains. Measuring sustainability requires the application of appropriate tools to effectively assess whether industries and societies are taking action to address the growing awareness of unstoppable climate change and resource depletion. In this context, environmentally friendly alternatives need to be developed [41] as well as the fulfilment of sustainability goals related to socio-economic issues [40]. In this sense, circularity aims to develop more cyclical frameworks in which resources are

maximized and waste is minimized [24,38,39,52]. This symbiosis between the two approaches could be considered as an effective strategy to develop new efficient production models [32,69,73].

Velenturf and Purnell [77] discussed the shared roots between the circular economy and sustainable development in the framework of systems ecology, including three main frameworks (social and individual well-being, environmental quality and economic prosperity) and 10 principles (i.e. reduce and decouple resource use or design for circularity). These authors also discussed the main differences between the sustainable development approach and the circular economy, while the

Abbreviations: FE, Freshwater eutrophication; FET, Freshwater toxicity; FPMF, Particulate matter formation; FRS, Fossil resource scarcity; GCP, Green Chemistry Principles; GW, Global warming; HCT, Human carcinogenic toxicity; HNCT, Human non-carcinogenic toxicity; IR, Ionizing radiation; LCA, Life Cycle Assessment; LU, Land use; ME, Marine eutrophication; PEF, Product Environmental Footprint; SOD, Stratospheric ozone depletion; TA, Terrestrial acidification; WC, Water consumption.

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former is mainly based on the well-being of society, economic growth and harmony with the environment, the latter is mainly based on the implementation of appropriate technological methods and innovations to improve economic growth through the integrated use of resources, waste valorization and the reduction of the harmful effects of emissions on the environment.

In terms of technological innovations, the improvement of technology and the optimization in the use of resources, favors a higher yield of the productive process, as well as a reduction of energy demand, this being one of the main hot spots in most bio-based projects [4]. In terms of performance, an improvement in the effective use of resources has a direct impact on the economic viability of the biorefinery process, a key aspect to favor its market penetration [16]. Innovative technologies that are expected to have a positive impact on the sustainability and efficiency of biorefineries include the following: the use of enzymatic and microbial models with genetically modified strains to increase the productivity of the fermentation process [18]; the use of specific catalysts adapted to the production processes to favor the reduction of process time and the increase in the selectivity and stability of the materials and products of the biochemical reactions [13]; the application of emission reduction technologies, such as carbon capture systems [6], and waste valorization techniques, such as the recovery of nutrients from wastewater [85]; and, finally, the use of advanced monitoring technologies to control and maintain process conditions that favor higher yields depending on the bio-based raw materials used as input resources [72].

The relevance of the commitment of all actors has also been reviewed by Trevisan et al. [74], as it has been discussed how a balanced and organized global framework not only promotes sustainable circularity, but also helps to better understand procedures, develop appropriate policies and funding, to enable the upgrading of systems towards greener processes. The reason behind stating “appropriate policies and funding” is given the fact that there are some regulatory and financial barriers that could affect the implementation of biorefineries, mainly related to feedstock availability and the consistent and cost-effective supply of biomass, as irregularity in availability could imply difficulties in reliable feedstock supply chains, more so compared to fossil resources, whose logistics are better established [27,4]. In addition, the low level of technological readiness for the development of bio-based processes could also imply two main barriers, one related to a greater difficulty in accessing public funding, given the lack of a proven track record, and the other to increased technological risks as a result of uncertainties regarding the good performance and reliability of new technologies [38,39,59]. On the other hand, the high time consumption of regulatory requirements and permit applications could reduce the progress of traditional production models, given the associated costs and time required to obtain permits from governments and public agencies [43,54].

Integrating the concept of circular economy as a driver of sustainable business models, Barros et al., [10] reported how circularity approaches can have an impact on strategic business areas ranging from product quality indicators to cost and environmental indicators, among others. The link between circularity and sustainable development could be addressed from early stages of the process under study, as it has been defined that up to 80 % of the degree of sustainability of a system could be influenced by preliminary decisions in the design phase. Indeed, circular economy practices have much to do with long-term growth and environmental quality, as concluded by several researchers who have assessed how circular strategies effectively reduce carbon emissions and thus contribute to achieving the Sustainable Development Goals (SDGs) [34,63,79,83].

This research work is framed within the combination of sustainability and circular economy approaches, delving into methodologies, strategies and indicators with the aim of illustrating how sustainable and circular procedures could be considered as effective and essential tools for the development of bio-based processes to ensure economic growth, environmental protection and social welfare. This manuscript pursues

three objectives: first, defining which are the most commonly used and required methodologies and frameworks to be applied in the assessment. Secondly, unlocking the potential of sustainable and circular evaluation approaches to drive greener, more efficient and responsible actions. Third, identifying the main issues and aspects that need to be addressed in order to develop a multidisciplinary framework. In order to assess these issues effectively, selected methodologies and approaches (LCA, PEF, Green Chemistry and circularity indicators) will be integrated with the aim of providing researchers, stakeholders and policy makers with a new methodological approach for the assessment of bio-based production models.

2. Methodological frameworks for the assessment of biorefineries

The following sections focus on the definition of each methodological approach, together with a review of research reports that have used them to assess biorefineries.

2.1. Life cycle analysis

A review of the literature over the last 10 years demonstrates the strong link between LCA methodology and biorefineries, based on the large number of research articles reporting on the assessment of bio-based models from an environmental perspective, especially for processes where bioconversion, fermentation and gasification are the core technologies. It should be noted that sustainability assessment involves the use of life cycle approaches to address environmental (E-LCA), economic (LCC) and social (S-LCA) perspectives. The main reason for this is the availability of well-developed guidelines, reported as ISO standards.

With respect to the E-LCA, the focus of this manuscript, the methodology is based on four steps defined by the ISO 14040–14044 guidelines [25]. The first one includes the goal and scope definition (i.e., *cradle to cradle* (full life cycle), *cradle to gate* (from extraction of raw materials to the factory gate), *cradle to grave* (from extraction to end-of-life management), and its combinations), and is standardized by ISO 14041. The second step is based on the collection of all necessary data, including inputs and outputs of materials, energy, emissions and waste to be treated. ISO 14042 provides guidelines for the development of the third stage, the environmental impact assessment, in which calculation methods for quantifying the impact categories must be selected. In this regard, the ReCiPe method and the CML are among the most widely used [1,8]. Other methods include USEtox, TRACI, IMPACT 2002+, EDIP, EPS, LIME, MEEUP, IPCC and Eco-indicator and [81]. These methods can be classified as midpoint or endpoint. The use of midpoint provides a more comprehensive analysis to reflect the relative importance of emissions and resource use, while endpoint is more valuable in cases where aggregation is desired [11,9]. Once the impact categories have been quantified, the final step is to interpret and analyze the results and develop sensitivity assessments around the main hotspots of the environmental profile (i.e. the main contributors to the impact categories) according to ISO 14043.

2.2. Product environmental footprint (PEF)

The PEF is a methodological approach developed by the EU Joint Research Centre to provide a procedure for estimating the environmental footprint of products, processes and organizations with harmonized methods [21,35,7]. Its guidelines were published in the Commission recommendations 2013/179/EU and 2021/2279/EU and are aligned with environmental claims and ecolabelling. These step-by-step rules are described at a much higher level of detail than the LCA methodology in ISO 14040–14044 and also provide clearer guidance. In this respect, defining a detailed roadmap to provide solid reference points could be detrimental to reducing flexibility. Some of the

main differences between HAP and LCA are listed below (Commission recommendations 2013/179/EU and 2021/2279/EU):

- (1) The functional unit should reflect the goal and scope of the system or product being assessed but should also be able to respond to the magnitude of the function (“*What*”), the duration or lifetime (“*How long*”), the level of quality (“*How well*”) and the quantity (“*How much*”). The functional unit must be able to provide information not only on the quantity but also on the quality of the product or process under analysis [53].
- (2) As far as the function of the system is concerned, PEF differentiated between “*in-house applications*” (i.e., identification of critical points or process optimisation) and “*external applications*” (i.e., product marketing or cooperation between life cycle stages).
- (3) The system boundaries in the PEF are not iterative and should be defined in the initial stages of the analysis. In addition, the processes included in the system boundaries must necessarily be divided into foreground and background. The International Reference Life Cycle Data System (ILCD) has recommended the use of this subdivision of system boundaries in some of its published manuals. However, the proposals have not yet been forced to conform to ISO standards.
- (4) Data requirements are also more limited in PEF, as foreground processes are expected to be built with primary data, while secondary data are only allowed for processes outside the control of the practitioner (i.e. background data). As the collection of detailed primary data implies a higher workload, a cut-off threshold of less than 3 % is allowed (which is lower than the value of 5 % allowed for LCA). This cut-off has been included in the latest version of the methodology.
- (5) The allocation of benefits for recycling is based on the “*circular footprint formula*”, which takes into account material recycling, energy recovery and disposal aspects.
- (6) Regarding the impact assessment, the PEF framework uses a set of impact methods for its midpoint impact categories whose indicators differ from those of the LCA. Those are shown in Table 1.
- (7) Unlike LCA, PEF requires separate reporting of fossil and biogenic emissions, indirect land use change, carbon storage and delayed emissions and emissions offsets. With respect to the robustness on capturing indirect environmental impacts, LCA focuses more on the direct impacts associated with the use of chemicals and resources, as well as the waste and emissions produced [23]. Indirect impacts are more difficult to quantify in terms of land use changes and water consumption, mainly due to the lack of qualified and accurate data [17,36]. However, the databases used for LCA, such as the EcoInvent database, are provided by region in most cases, so that they are adapted to the geographical location, in which past and present indirect impacts are included (as the EcoInvent database is regularly updated) [37,55]. To define and analyze impacts in the immediate future, the use of prospective assessment could be of great help [65]. On the other hand, it should be kept in mind that system boundaries also influence the estimation of indirect environmental impacts; for example, if a “*cradle-to-gate*” approach is considered (from raw material extraction to product), background activities related to land use changes are taken into account, but if a “*gate-to-gate*” approach is assessed, land use may not be fully addressed in the analysis and thus may not affect the environmental profiles [60]. In this sense, the integration of indirect environmental impacts depends not only on the robustness of the LCA methodology, but also on the type of assessment and assumptions considered for the analysis.

Table 1

PEF impact categories, including its indicators, units, recommended calculation models and degree of robustness (PEF methodology).

PEF category	Indicator	Unit	Recommended characterization method
Climate change, total	Global warming potential	kg CO ₂ eq.	IPCC 2013
Ozone depletion	Ozone depletion potential	kg CFC-11 eq	Steady-state ODPs
Human toxicity, cancer	Comparative Toxic Unit for humans	CTUh	USEtox model 2.1
Human toxicity, non-cancer	Comparative Toxic Unit for humans	CTUh	USEtox model 2.1
Particulate matter	Impact on human health	Disease incidence	PM method recommended by UNEP
Ionizing radiation, human health	Human exposure efficiency relative to U ²³⁵	kBq U ²³⁵ eq	Dreicer et al., 1995
Photochemical ozone	Tropospheric ozone concentration increase	kg NMVOC eq	LOTOS-EUROS model
Acidification	Accumulated Exceedance	mol H ⁺ eq	Accumulated Exceedance
Eutrophication, terrestrial	Accumulated Exceedance	mol N eq	Accumulated Exceedance
Eutrophication, freshwater	Fraction of nutrients reaching freshwater end compartment	kg P eq	EUTREND model
Eutrophication, marine	Fraction of nutrients reaching freshwater end compartment	kg N eq	EUTREND model
Ecotoxicity, freshwater	Comparative Toxic Unit for ecosystems	CTUe	USEtox model 2.1
Land use	Various (soil quality index, biotic production, erosion resistance, mechanical filtration and groundwater replenishment)	Various (Dimensionless, kg biotic production, kg soil, m ³ water and m ³ groundwater)	Soil quality index based on LANCA
Water use	Use deprivation potential	m ³ world eq	Available WATER REmaining (AWARE method)
Resource use, minerals and metals	Abiotic resource depletion	kg Sb eq	CML 2002
Resource use, fossils	Abiotic resource depletion	MJ	CML 2002

2.3. Requirements embedded in certification schemes (CS): sustainability and circularity

The use of single-score indicators allows the environmental analysis to be extended to cover additional aspects that could have a significant impact on environmental sustainability and circularity, such as waste management strategies, which are not covered by the other methodologies included in this research. However, the selection of indicators needs to be adapted to the minimum requirements of sustainability and/or circularity. For this reason, the use of criteria from certification schemes can help to correlate indicators with legislation and provide an adequate quantitative assessment for the certification of products from biorefineries. The basic information used to establish the outstanding criteria was taken from the Standards Map, which is the largest database

of sustainability certification schemes, with a total of 340 certification schemes organised in 19 sectors. This unmanageable number for data collection and analysis requires selective screening to filter out the most appropriate certification schemes to be applied to the base case scenarios. Taking into account the case studies selected for evaluation and comparison of methodologies, two sectors were selected: agriculture (according to the origin of raw materials) and energy. Five additional keywords were used in the database to follow up the selection to ensure that:

- (1) Certification schemes directly applicable in European countries.
- (2) Applicability within the chain of custody, which should cover the manufacturing stage.
- (3) Certification was chosen as the main selection criterion, with accreditation, benchmarking and guidelines as secondary criteria.
- (4) There is a third-party verification or auditing of the certification scheme.
- (5) Recognition by other standards or institutions such as the International Social and Environmental Accreditation for Labelling Alliance (ISEAL), the Consumer Goods Forum Sustainable Supply

Chain Initiative (CGF SSCI) and the European Feed Manufacturers Federation (FEFAC).

Under the minimum conditions mentioned above, the number of certification schemes was reduced to 22. However, not all of them were within the scope of the research and a final critical analysis was required for the final selection of suitable certification schemes. Those relating to other sectors (e.g. textiles and marine), specific products (e.g. cotton and soy) or which had expired were excluded from the analysis. After the final selection, the 10 certification schemes shown in Table 2 were selected. All of them were afterwards compared considering four of the nine principles described in the *Standards Map* database. Criteria for “animals”, “biodiversity”, “forest” and “soil” were neglected as they could not be measured for the manufacturing operation of industrial processes using mass and energy balances (the type of data available in this research for comparing methodologies). In order to evaluate the scenarios proposed in this research report, 28 indicators have been selected for each of the criteria defined in Table 3.

2.4. Green Chemistry principles: Green Index (GI)

The aim of Green Chemistry (GC) is to design products and

Table 2
Principles and criteria of Standards Map correlated to the 10 selected certification schemes.

Principle	Criteria	Global GAP Crops	LEAF Marque	ProTerra Europe	Sustainability Initiative of South Africa - SIZA	Amaggi ORIGINS FIELD	ISCC EU	Forest Stewardship Council	Fairtrade International	Rainforest Alliance	The Gold Standard
Waste	Treatment and use of solid waste	X	X	X	X	X	X		X	X	
	Reducing solid waste volumes	X			X	X	X			X	
	Reuse and recycle solid waste	X	X	X	X	X	X	X	X	X	
	Air quality / pollution	X	X	X	X						
Energy	Energy consumption	X	X	X	X	X	X		X	X	
	Reduce the use of energy resources	X	X	X	X	X	X		X	X	X
	Use of renewable energies including solar, wind, etc.	X		X	X		X		X	X	
Climate	Quantifying GHG emissions			X	X		X	X	X		X
Water	Water resources use and consumption	X	X	X	X	X	X		X	X	X
	Water dependencies and water scarcity	X	X	X	X	X	X			X	
	Surface and ground water pollution	X	X	X		X	X		X	X	
	Water reuse & recycling	X	X		X		X		X	X	
Inputs	Restricted use of resources with impact on human health and the environment					X			X	X	
	Chemical application records and reduction	X	X	X	X	X	X		X	X	

Table 3
List of indicators per principle and criteria chosen from certification schemes.

Principle	Criteria	Indicator	Description	Unit	Indicator	Description	Unit
Waste	Treatment and use of solid waste	Waste to landfill	The amount of solid waste that is inadequately managed	kg waste going to landfill/kg of product	Waste management	Amount of waste with additional treatment	kg of waste treated on site/kg of waste produced
	Reducing solid waste volumes	Minimization of waste	Measurement of the efficiency of the process to minimize derivatives	kg solid waste/kg product	Process productivity on waste	Amount of waste produced per input material	kg waste/kg of input material
	Reuse and recycle solid waste	Recovery of waste	Amount of waste biomass recovered	Tons of input waste biomass/kg product	Recycling rate of waste	Amount of waste used as resource	kg of input waste/kg of product
	Air quality / pollution	Ozone depletion (LCA)	Potential of destructing ozone layer	kg CFC ₁₁ eq/kg product	Particulate matter emissions	Emission of solids to the air	kg PM2.5 eq/kg product
Energy	Energy consumption	Energy intensity	Amount of energy required in the process	TJ	Energy efficiency	Amount of energy required per product	kWh of energy required/kg of product
	Reduce the use of energy resources	Efficient energy use	Process capacity to enhance the adequate use of energy resources	MWh/kg of product	Virgin materials	Consumption of virgin materials	Tons of virgin materials/total inputs
	Use of renewable energies including solar, wind, etc.	Energy from biomass	Evaluation of the process capacity for energy self-consumption	% HP steam	Renewable energy	Amount of renewable energy used	% of renewable energy per total energy required
Climate	Quantifying GHG emissions	Identification of pollutant resources	Measurement of the global warming potential of the process	kg CO ₂ eq./kg product	Direct and indirect GHG emissions	Percentage of GHG direct emitted	kg CO ₂ eq. direct emitted/ total kg CO ₂ eq.
Water	Water resources use and consumption	Water consumption (LCA)	Volumetric amount of water required	m ³	Freshwater consumption	Amount of freshwater consumed per product	m ³ freshwater/kg product
	Water dependencies and water scarcity	Water scarcity (PEF)	Potential of water deprivation in the process	m ³	Reclaimed water	Amount of reused water in the process	m ³ reused wastewater/ m ³ input water
	Surface and ground water pollution	Quantification of emissions (wastewater)	Identification of the emission flows to the water sector	m ³ wastewater/kg product	Water quality of receiving bodies	Identification of the composition of the wastewater flows	kg P eq./kg product
	Water reuse & recycling	Avoidance and reduction of effluents	Process capacity to reuse the process flows	m ³ of reclaimed water/kg product	Reclaimed water	Identification of the productivity of the process to reduce water consumption	% reclaimed water
Inputs	Restricted use of resources with impact on human health and the environment	Consumption of resources	Analysis of the efficiency on the use of chemicals	kg resource/kg product	Ecosystem damaging chemicals	Evaluation of depletion of abiotic resources by the use of chemicals	kg Sb eq./kg product
	Chemical application records and reduction	Recycled chemicals	Capacity of the process to reuse chemicals on the process	% of recycled chemical	Amount of chemicals	Input chemicals required on the process	kg of chemicals/kg of product

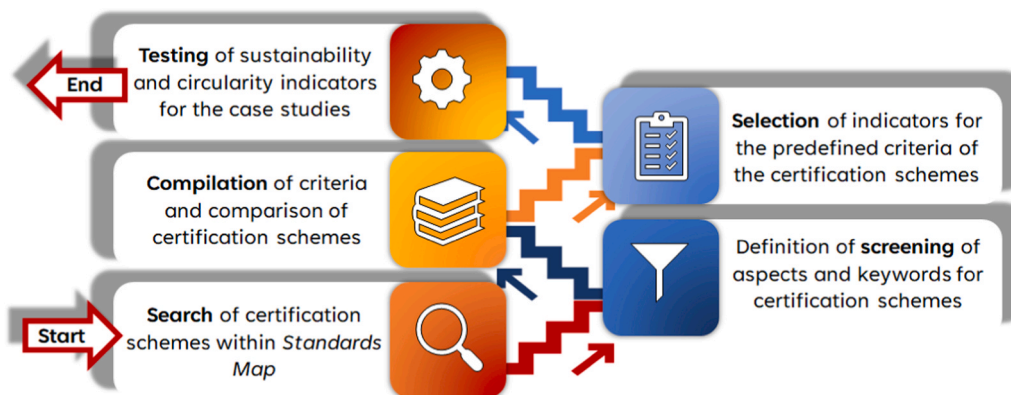


Fig. 1. Methodological approach to identify and assess sustainability and circularity criteria.

manufacturing processes with the lowest possible impact on the environment and on human health. The development of safer and more efficient processes are the goals of GC, together with the encouragement of opting for the lowest waste production [48]. Under these premises, GC is based on 12 principles, which are listed and defined in the [Supplementary Material](#) – Green Index. In terms of quantification and scoring, some of the equations are derived from the QA principles, but others come from Pinto et al., [56], with a total of 15 principles to be quantitatively scored. The final Green Index score is calculated by summing each of the principles, which are normalized to a value between 0 and 1. Thus, the score ranges from 0 to 15, with 0 being the worst outcome (an unsustainable process) and 15 being the ideal value (a sustainable model). In order to assess the intermediate values, a color code was used to qualitatively represent the sustainability potential of the processes evaluated according to the Greenness Grid methodology: 0–3 (unsustainable, brown color), 3–6 (critical, orange color), 6–9 (on path, yellow color), 9–12 (potential sustainable, blue color) and 12–15 (sustainable, green color).

3. Methodologies under the spotlight: Application in three biorefinery approaches

To identify the adequacy, constraints and benefits, the aforementioned methodologies are being applied to three biorefinery scenarios previously developed and modelled here: (S01) valorization of apple vinasses for the production of bio-hydrogen and biogas using a two-stage fermentation, (S02) resveratrol production through valorization of viticulture residues and (S03) extraction of dietary fiber using chickpea hulls residues. Fig. 2 shows an overview of the process schemes for each of the selected scenarios. The applicability of the LCA, PEF, GI and single-score circularity and sustainability indicators is assessed across facilities belonging to different value chains. While the valorization of apple stillage can be integrated into energy production, the treatment of chickpea hulls covers the food chain, and the production of resveratrol

has a potential application in the cosmetics and pharmaceutical sectors.

3.1. Description of scenario S01: Apple vinasses to bio-hydrogen through dark fermentation

Scenario S01 consisted of a 7-step process producing two energy bioproducts, hydrogen and biogas, from the valorization of apple vinasses with 60 % solids content from an ethanol distillery at 100 °C. The liquid stream was converted by a two-step biological process under anaerobic conditions: dark fermentation followed by anaerobic digestion. This plant was modelled and described in the work of [22], where the production capacity was considered to be 2000 t/year. The authors carried out a Life Cycle Assessment (LCA) and found that the energy demand is the main critical point of the environmental profile obtained, with an average contribution of 63 % considering all the impact categories, while the use of chemicals implies an average of 26 %, much lower. The remaining impact was attributed to direct emissions to air and water from the process. An important observation is that the high temperature of the stillage and the control of the heat exchange within the system resulted in a thermal energy free process, which implies a strong relationship of the operation with the electricity profile of the country of implementation.

3.2. Description of scenario S02: resveratrol production valorizing grape must residues

Scenario S02 involved the production of resveratrol using grape must as the bio-based feedstock, sourced from the wine sector. The wine production process requires four main stages: destemming and crushing of the grapes, fermentation, pressing, aging and stabilization of the wine to improve its quality. These stages produce two main residues: grape must at the pressing stage and less wine at the final stage. In this case, grapes should be considered as having the ideal composition of fermentable sugars to be used for valorization in a biorefinery approach.

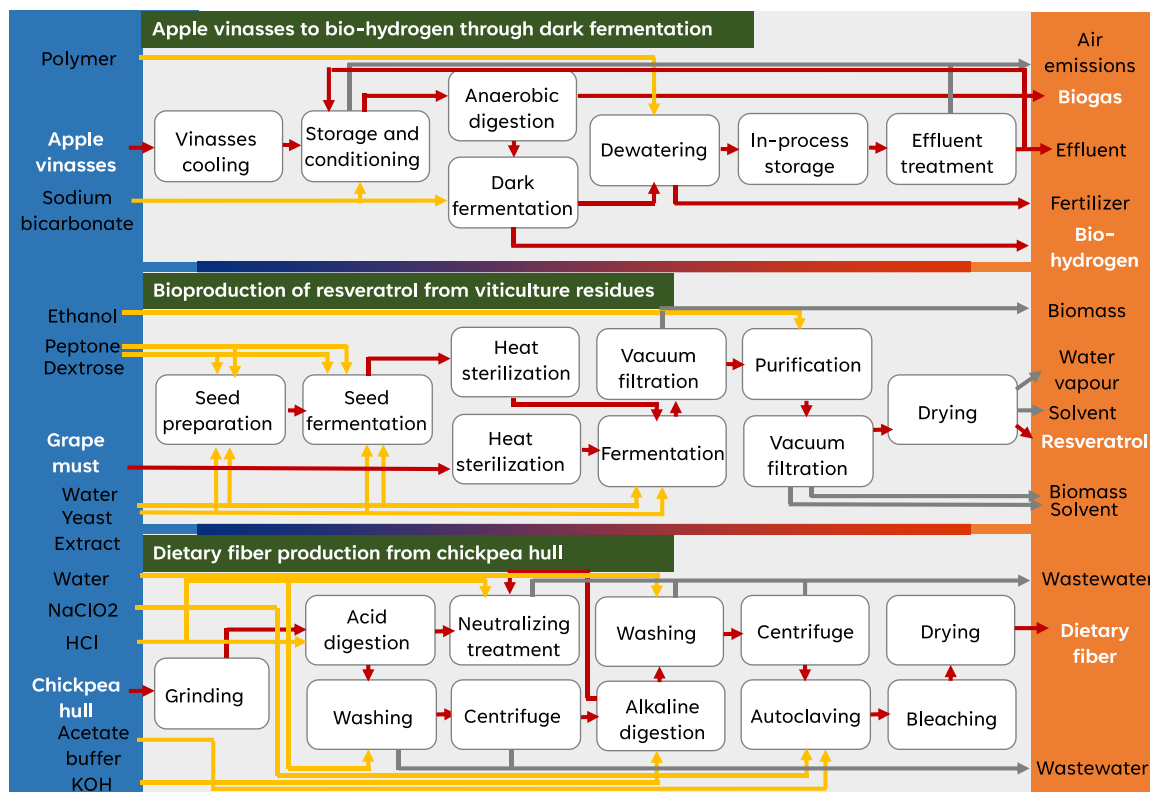


Fig. 2. Overview of the inputs, outputs, and process stages of the biorefinery scenarios selected for methodology assessment.

It was used for the production of resveratrol, which requires two main process steps, taking into account that no pre-treatment is required as it has a composition of fermentable sugars suitable for direct application, fermentation and post-purification. The downstream involves the development of three main process steps: filtration, ethanol purification and spray drying to obtain a final powder with 95 % purity of resveratrol. Process modelling, techno-economic and environmental life cycle assessment of the process have been previously developed in the manuscript and conclude that the process is economically feasible and that electricity and peptone, which is a nutritional supplement to the fermentation process, are the main hot spots of the environmental profile. In fact, energy consumption implies an average share (for all impact categories) of 55 % of the profile and 53 % corresponds to electricity, while the contribution of chemicals in the LCA was much lower (~45 %).

3.3. Description of scenario S03: Dietary fiber from chickpea hulls valorization

Scenario S03 corresponds to the valorization of chickpea hulls to obtain dietary fiber based on the work by Rebollo-Leiva et al. [61]. The process starts with a grinding step to homogenize the size of the biomass, then the particles are digested in acid media. The resulting stream is filtered, and the solids are washed and centrifuged. The dewatered clean husks are then hydrolyzed under alkaline conditions. As in the previous reaction step, the effluent is filtered, washed and centrifuged. After this alkaline hydrolysis, the remaining solid shells were autoclaved, bleached to improve the color of the powder and dried. The final product had a total fiber content of 78 %. The effluent from all these stages was first neutralized and then sent to an external operator. In terms of LCA characteristics, the environmental analysis was performed for a cradle-to-gate biorefinery using a 1 kg dietary fiber product as the functional unit. The LCA results showed that alkaline digestion, bleaching and chickpea cultivation were the most important contributing steps according to the impact category analyzed. However, as in the case of apple vinegar and grape pomace, energy consumption is a factor of concern (average representativeness of 13 %). However, the use of potassium hydrogen, which is required during alkaline digestion, significantly outweighs the energy impacts. Due to this chemical and others used in acid fermentation (i.e. HCl) and bleaching, the environmental profile was mainly characterized by chemical inputs (~87 %).

4. A critical appraisal of methodologies

4.1. Change of scope and functional unit between LCA and PEF

This section analyses the results obtained using the PEF methodology for the selected scenarios with minor modifications that address the specificities of each case study. Firstly, the background processes have been accounted with an allocation at the point of substitution (APOS), while the functional units (FU) have been modified to address the *What-How Long-How well-How much* structure defined by the PEF. Bearing this in mind, the FU for S01 was considered to be “the valorization of apple vinasses for the annual operation of the facility to transform 2000 t/year with a solid content of 60.32 %”, for S02 “the production of 1 kg of resveratrol for the cosmetics industry with a production capacity of 374.36 kg of grape must waste” and for S03 “the production of 1 kg of dietary fiber product with a purity of 78 % from chickpea hulls with an annual operation of 40,000 tons”. Furthermore, this was considered an “in-house application” considering the function of the systems, as the LCA and PEF were compared in terms of hotspots. The impact values obtained by the PEF methodology are depicted in Table 4 for S01, S02 and S03.

Table 4

PEF scores obtained for S01, S03 and S03 alternatives.

Impact category	Unit	S01	S02	S03
CC	kg CO ₂ eq	2.36·10 ⁴	142.36	3.95
OD	kg CFC ₁₁ eq	0.00	7.59·10 ⁻⁶	9.44·10 ⁻⁷
IR	kBq U-235 eq	5.12·10 ²	8.62	0.44
POF	kg NMVOC eq	33.60	1.03	1.92·10 ⁻²
PM	disease increase	8.00·10 ⁻⁴	2.91·10 ⁻⁶	3.83·10 ⁻⁷
HNCT	CTUh	8.25·10 ⁻⁵	5.30·10 ⁻⁶	3.62·10 ⁻⁷
HCT	CTUh	2.40·10 ⁻⁶	2.23·10 ⁻⁸	3.25·10 ⁻⁹
AC	mol H ⁺ eq	128.94	0.94	3.15·10 ⁻²
FE	kg P eq	8.26	0.04	1.28·10 ⁻³
ME	kg N eq	18.05	0.20	1.59·10 ⁻²
TE	mol N eq	340.99	1.69	9.39·10 ⁻²
FET	CTUe	1.39·10 ⁵	1.74·10 ³	3.53·10 ³
LU	Pt	2.57·10 ⁴	1.43·10 ³	110.6
WU	m ³ depriv.	6.80·10 ³	2.05·10 ³	3.68
FRS	MJ	3.03·10 ⁵	1.59·10 ³	57.17
MRS	kg Sb eq	0.00	1.23·10 ⁻⁵	2.26·10 ⁻⁵

4.2. Similarities and differences in the characterization profile between LCA and PEF

Regarding the PEF results obtained for S01, the electrical demand is the main hotspot with an average contribution of 55 %, which is lower than that obtained in the LCA (63 %). As for the chemical demand, its contribution amounts to 30 %, which is higher than that of the LCA (26 %). Given the differences obtained for these contributions to the total impact, it could be assumed that the PEF pays more attention to direct emissions to air and water (~15 % compared to ~11 % in the LCA), while giving less value to background processes. The justification for these possible differences could be the use of different characterization factors, the substances considered and the use of cut-off criteria (related to LCA) instead of APOS (related to PEF). The use of APOS or cut-off criteria does not seem to be relevant for the impact scores obtained, with the exception of five categories: freshwater (7.3 %) and marine ecotoxicity (6.7 %), human carcinogenic toxicity (5.8 %), land use (17.6 %) and mineral resource scarcity (27.8 %). While the latter reaches a value of about 28 %, the other 11 categories have deviations of less than 5 %.

In the case of S02, the outcomes of the PEF are still in line with those of LCA since the average contribution of chemicals (~37 %) is higher than that of energy (~47 %). This situation is also confirmed when analyzing by category, as 12 out of 18 for ReCiPe and 8 out of 16 for PEF show a higher impact for energy. However, the number of categories supporting the predominance of energy is much higher for LCA than for PEF. Therefore, the choice of PEF or LCA as a methodology can be critical not only for providing specific quantitative results, but also for formulating recommendations and conclusions. As for scenario S01, scenario S03 does not show large changes in the results obtained for LCA and PEF. In fact, the average deviation of the chemical to energy ratio is less than 2 %. As the process is based on alkaline acid digestion (mainly based on mixing), direct emissions have not been inventoried. Therefore, unlike the S01 process, the profile is only defined by the impact of the upstream processes. Thus, the difference could be given by two aspects: the use of cut-off and APOS allocation approaches and the substances characterized by the respective factors of each method.

4.3. Comparison of impact categories with normalization

Analyses of the impact results using the individual methodologies have revealed differences in the scores obtained. Differences in the units of measurement of the impact categories of each method made it impossible to establish a common framework for comparison. Although both PEF and LCA can analyze the same level of the environmental cause-effect chain (MidPoint), the method selected for the LCA may limit the comparability between the methodologies. The ReCiPe 2016

Midpoint (H) V1.07 / World (2010) H chosen for the LCA addresses most of the environmental aspects of PEFs, including global warming potential, eutrophication, resource use, toxicity and water use. However, it is not possible to make a direct comparison between them as only four of the 16 PEF impact categories (climate change, ozone depletion, freshwater eutrophication and marine eutrophication) are measured in the same way as ReCiPe.

In order to identify variations in the results, normalization of the values has been developed that takes into account the relative contribution of each impact category to the overall normalized impact. In the case of the PEF and the production process of apple vinasses, the three most important categories were FE (~20 %), FRS (~18 %) and FET (~13 %). In contrast with these outcomes, the LCA methodology reported HCT (~46 %), FE (~13 %) and FET (~9 %) were the top three categories. While ecotoxicity appears to be an important environmental issue for both methods, PEF gives also value to resource use. The relative relevancy between each of the categories of the methodologies are depicted on Fig. 7, being (A) the one relative of the valorization of apple vinasses, (B) the characterized of grape must and (C) representing the chickpea process scheme. Fig. 7A shows how the LCA gives more importance to three categories (HCT, SOD, and IR). For the HCT category, it represents 0.55 % of the total impact when using PEF and reaches 46.2 % for LCA and gives a variance of 98.8 % as shown in Fig. 3A.

Similarly, the resveratrol or S02 production process showed different rankings for each method. FE (9 % for LCA and 7 % for PEF) and FET (14 % for PEF) were again among the most concerning categories. HCT (32 %) also ranked first in the LCA. However, in the case of resveratrol, the WC category is in the top three in both cases. Regarding the distribution of the importance of the categories between the methods, Fig. 3B also shows a higher relevance for HCT, SOD and IR in LCA. The process S03 reported two main categories: HCT (with a representativeness of 55 % for LCA) and FET (in this case 91 % for PEF). Other categories such as freshwater eutrophication and freshwater ecotoxicity were

significantly under-represented in the LCA (<8 %). In PEF, human non-carcinogenic toxicity and fossil resource scarcity ranked second and third, but with much lower representativeness (<1.7 %). Therefore, for biorefinery processes as different as S01, S02 and S03, PEF gives more and more importance to the FET and FE categories (in some cases HNCT, FRS and WC). On the other hand, the most relevant categories for LCA would be HCT and FE. Regarding the results of Fig. 3C, PEF provides a higher contribution in the categories of FET, MS, HCT, HNCT and MRS (differences of 93 %, 17 %, 37 %, 79 % and 99 % respectively). The comparison of the three profiles of Fig. 2 may indicate that each method ranks the weight of the most relevant category in a different way.

4.4. Are characterization factors relevant comparing LCA and PEF methodologies?

The review of the characterization factors of the main substances involved in the profile of each impact category is shown in the [Supplementary Material- LCA](#). According to the results obtained, there is no clear trend in the profile and therefore the factors are sometimes higher for ReCiPe and sometimes higher for PEF. In addition to the factors, the quantification of the substances is also relevant for the final profile. To illustrate this conclusion, further analysis and discussion of the factors that are most unfavorable to the environmental profiles is carried out.

Electricity requirements were the main resource used in 12 of the 15-background input processes of S01 and thus became the main environmental contributor to the system. For this purpose, the European medium voltage electricity production was used as a reference process to show how the ReCiPe and EF Method 3.0 (adapted) V1.03 characterization factors influenced the results. For this purpose, the electricity system was analyzed considering the characterization of inventoried substances for the four MidPoint impact categories using the same indicator value (i.e., climate change is expressed in kg CO₂ eq) in both methodologies. For each impact category, the two most representative

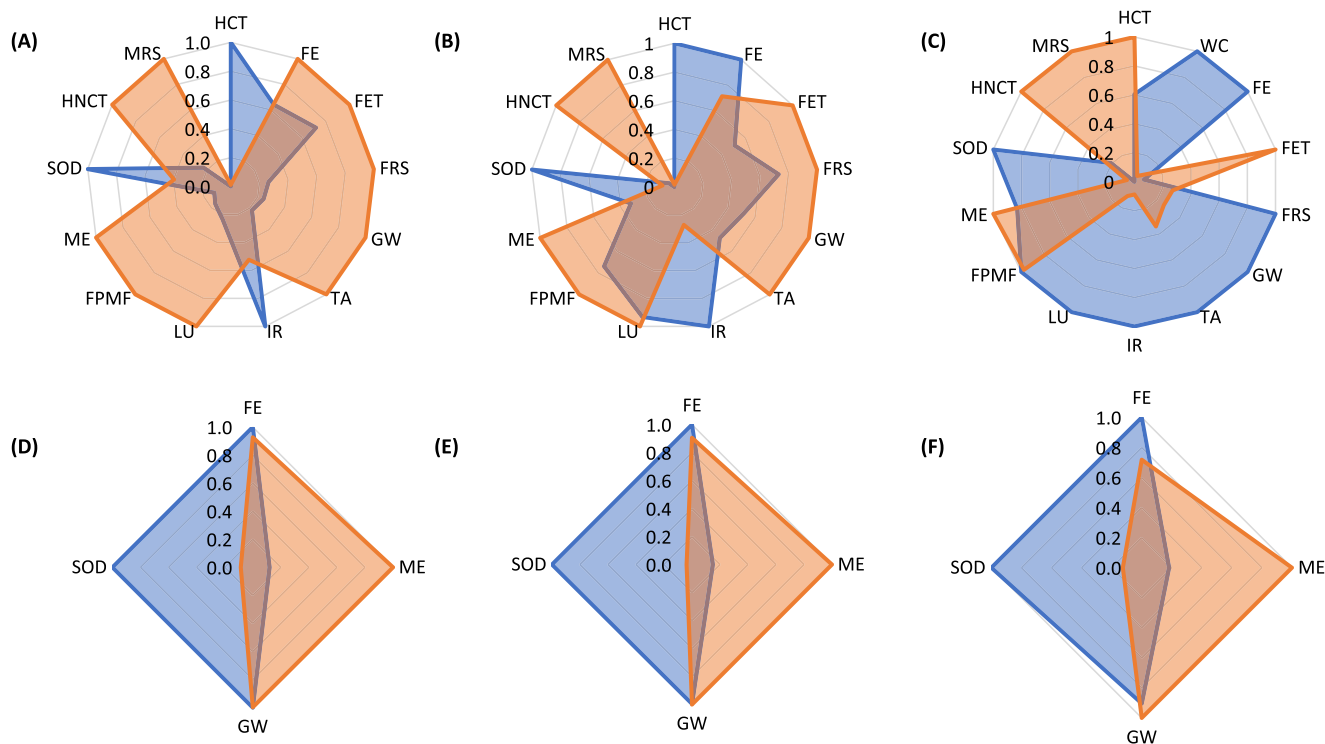


Fig. 3. Overview of the relative relevancy between each of the categories of the methodologies. (A) valorization of apple vinasses process; (B) production of resveratrol by valorizing viticulture-related residues and (C) extraction of dietary fiber using chickpea hulls residues. Comparison of the PEF and LCA MidPoint characterization outcomes for the (D) valorization of apple vinasses process; (E) production of resveratrol by valorizing viticulture-related residues and (F) extraction of dietary fiber using chickpea hulls residues. (Color code: blue is LCA, and orange is PEF).

substances were selected. For example, carbon dioxide and methane were the most relevant substances for LCA and PEF in the climate change category. Although the substances were consistent for this category, the considerations between the methodologies were not always the same. In the marine eutrophication category, emissions of phosphates to water and phosphorus to soil were relevant for PEF. However, the second most relevant element in the LCA was no longer phosphorus but chemical oxygen demand (COD) emissions.

In Fig. 3D, the result of the relative environmental characterization with LCA and PEF for the apple vinasse process, the categories global warming and freshwater eutrophication show little variation (0.25 % and 7.31 % respectively) between the methodologies. This is due to the use of similar characterization factors for the main pollutants. However, for stratospheric ozone depletion and marine eutrophication the differences reach 91 % and 88 % respectively. The former is due to emissions of nitrous oxide to the atmosphere from electricity generation. The PEF methodology does not have a characterization factor for this substance, which is one million times higher in quantity than the other two selected substances in the inventory. For marine eutrophication, the differences are mainly due to the characterization factors for nitrogen oxides to air and nitrates to water. This is because these values are significantly higher for PEF than for LCA. Fig. 3E and 3F show an analogous profile to Fig. 3D.

Although the electrical profile of the research by Arias et al. [3] is from Portugal and not from Europe, the differences in the characterization for the substances involved in each of them are negligible. Therefore, the biohydrogen-biogas and resveratrol production processes differ in the consumption of the type of chemicals. However, there is another common aspect to consider when analyzing S01 and S02. Both processes are characterized by a predominance of energy use in their environmental profile. This is not the case for the fiber production process, as the use of renewable energy reduces the relative contribution of energy use to below 13 %. Therefore, the characterization profile between PEF and LCA is modified by the burdens of other substances released to the environmental media as well as their characterization factors.

4.5. Analyzing how certification scheme requirements contribute to the environmental profile of systems

LCA, PEF, GCP and the use of indicators share a distinct characteristic: they all provide a multi-criteria analysis. While PEF and LCA are methodologies whose guidelines have already been influenced by legislation or standards, the level of development of the GCP and indicators is far behind. However, the use of GCP and indicators may have some advantages over the others. Unlike LCA and PEF, the GCP provides an overview of the extent of process sustainability and ranks facilities or processes accordingly. In contrast, LCA and PEF require a baseline scenario or product to compare impacts and show whether a sustainability pathway has been followed. As PEF is perhaps the least flexible of the above methodologies, the use of indicators can give its users more freedom. In this sense, practitioners can decide whether to perform a single score analysis, define the analysis system from a quantitative and qualitative perspective, considering not only sustainability aspects but also those related to performance and circularity, and correlate legal requirements with measurable aspects.

Nowadays, certification schemes rely on the use of indicators to enforce the use of their criteria and requirements for companies or institutions interested in accreditation, certification or verification. However, although many environmental, social, governance and management aspects are covered, the indicators used are almost exclusively qualitative. Exceptions could be identified for the calculation of greenhouse gas emissions (i.e. Better Biomass is one of the certification schemes that includes this estimation) or the use of equations in material recycling (i.e. the FSC certification scheme). The introduction of the quantitative indicator framework can contribute to the pursuit of a more

impartial certification process, as criteria can be assessed numerically from company data. There is one particular aspect that certification bodies should consider for the future selection of indicators within a specific sector: the clear definition of the criteria and requirements that form the basis for the development of appropriate indicators. Comparability of certification schemes is a difficult task due to the lack of understanding of principles, criteria and requirements without a common definition. At present, indicators can be divided into three different categories: key performance, sustainability and circularity. In this sense, the use of indicators can not only be a simple and comprehensive way to measure the sustainability of a process from its early design stages, but also provide knowledge about its circular behavior. Therefore, the use of indicators can be useful to get an overview of a process for which data is limited or to provide additional information to existing PEF and LCA methodologies (i.e. circularity). The use of indicators is expected to be useful in decision making, both at an early stage of the process and when it is well developed, to identify where action should be taken to improve its sustainability and circular potential. In addition, another important aspect of the use of indicators is their ease of calculation and interpretation, which facilitates progress in the performance, quality and cost-effectiveness of the assessed processes.

4.6. How are the indicators beneficial?

This section develops an overview on the use of the selected indicators in Table 3, as well as their appropriate analysis. Regarding the "waste" principle, some of the indicators should be interpreted jointly, such as "minimization of waste", "recovery of waste", "recycling rate of waste" and "waste management", which should be interpreted together, giving more value to the ability of the process to recover waste than to the amount of waste finally generated. The reason for this can be clearly seen when looking at case study 2, where resveratrol is produced, as a large amount of waste from the wine value chain is used to generate a proportionally small amount of product, albeit with high added value. In this way, a double objective is being achieved, revalorizing a compound and, subsequently, still having the option of sending this biomass for energy recovery (Table 5). In relation to this valorization strategy, the indicator "waste to landfill" could be associated, which should be as low as possible, or even with a value of 0 since waste management in landfills is considered an unsustainable practice as well as being non-circular. On the other hand, another essential indicator to evaluate is the "process productivity over waste", as it is a value that provides the capacity of the process to use the residual resources to generate value, which is associated with the reduction of virgin resources, thus avoiding their overexploitation. Analogous to the main aspects of the energy principle is the "input" principle, which focuses more on the use of chemicals/raw materials in the process. To assess efficiency and productivity on these requirements, indicators such as "chemical quantity", which measures the ratio between the total amount of chemicals needed per product generated, which should be as low as possible, or the "capacity of the process to promote recycling" should be evaluated, as production schemes should promote the reuse of resources to enhance the circular economy and move forward from traditional linear production models.

The scores obtained for the scenarios under assessment are depicted in Table 5 and, as can be seen, provide an overview to define where to focus in order to increase the circularity and sustainability potential of the bio-based process. For example, a positive aspect of all the scenarios is that none of them sends solid waste to landfill, thus avoiding the negative effects caused by this type of waste management. In the case of S01, no solid waste or wastewater is produced in the process while in the case of S02, the amount of waste produced is 0.17 kg/kg of product, which is quite low but still an issue for improvement, as it is not recycled in the process, as shown by the results of the "recycling rate of waste" indicator. On the contrary, Scenario S03 achieves a higher value of 0.97 kg/kg, primarily from the wastewater generated in the process.

Table 5
Scoring of the indicators to assess the scenarios under a sustainable and circular perspective.

Principle	Indicator	S01	S02	S03	Indicator	S01	S02	S03
Waste	Waste to landfill	0	0	0	Waste management	0	0	0
	Minimization of waste	3.03	3.22	1.95	Process productivity on waste	0	0.17	0.97
	Recovery of waste	$3.0 \cdot 10^{-3}$	0.37	$1.9 \cdot 10^{-3}$	Recycling rate of waste	0	0	0
	Ozone depletion (LCA)	$9.46 \cdot 10^{-9}$	$2.04 \cdot 10^{-4}$	$6.87 \cdot 10^{-6}$	Particulate matter emissions	$3.51 \cdot 10^{-5}$	0.23	$6.41 \cdot 10^{-3}$
Energy	Energy intensity	0.07	1.59	$3.19 \cdot 10^{-3}$	Energy efficiency	0.03	268.38	0.89
	Efficient energy use	$2.93 \cdot 10^{-5}$	0.27	$8.88 \cdot 10^{-4}$	Virgin materials	0.002	0.33	0.02
	Energy from biomass	0	0	0	Renewable energy (%)	0	0	100
Climate	Identification of pollutant resources	$3.59 \cdot 10^{-2}$	148.08	3.44	Direct and indirect GHG emissions	0.02	0.01	0
Water	Water consumption (LCA)	269.17	47.87	0.18	Freshwater consumption	0.00	0.17	0.11
	Water scarcity (PEF)	6800.57	2050.42	3.68	Reclaimed water	1.00	0.70	0.02
	Quantification of emissions (wastewater)	$5.18 \cdot 10^{-4}$	0.09	0.11	Water quality of receiving bodies	$1.35 \cdot 10^{-5}$	0.05	$1.28 \cdot 10^{-6}$
	Avoidance and reduction of effluents	$6.18 \cdot 10^{-3}$	166.69	$2.10 \cdot 10^{-3}$	Reclaimed water (%)	100	70	1.86
Inputs	Consumption of resources	3.04	374.36	116.35	Ecosystem damaging chemicals	$3.03 \cdot 10^{-9}$	$4.95 \cdot 10^{-5}$	$2.26 \cdot 10^{-5}$
	Recycled chemicals (%)	0	80	0	Amount of chemicals	$7.01 \cdot 10^{-3}$	0.05	3.45

Another important factor to evaluate is the energy intensity of the process, as well as the energy sources used, with renewable resources being preferred to move towards more sustainable and circular systems. For example, in the case of S02, the energy intensity and energy efficiency are quite intense and significant (bearing in mind that energy efficiency is measured in kWh/kg of product, so the higher the value, the higher the energy required). The fact that a small amount of product is obtained per raw material, as shown by the "Consumption of resources" indicator: 374.36 kg of resources are needed to produce 1 kg of resveratrol, also has an impact on the energy requirements, as well as on the necessary equipment (i.e. fermenters, centrifuges, filtration units, spray dryers, etc.), which are energy intensive. However, in the research carried out by Arias et al. [3], it was shown that the choice of renewable resources could have a significant benefit in terms of the sustainable and circular potential of the process, due to the reduced use of fossil resources and the reduced environmental impact. Therefore, it could be concluded that in order to move towards more circular bio-based processes, the "Renewable energy" indicator should be as high as possible, as it brings benefits compared to other pillars of sustainability, while at the same time the "Virgin materials" indicator should also be as low as possible, considering not only energy resources but also material resources. In this particular case, S01 receives the lowest score because it is able to treat a total of 2000 tonnes of apple vinasses per year, while using only 4.62 tonnes of polymer and 4.29 kg of sodium bicarbonate, which are the resources of "non-virgin materials". The authors assume that the main inputs used in the development of bio-based process schemes are non-virgin materials, as they are all waste streams from other processes: apple vinasses from bioethanol production, grape must from wine production and chickpeas hulls from flour production.

It is worth noting that, despite the good scores achieved by S01, it is the scenario with the highest water consumption and the greatest impact on water scarcity. The reason for this high score compared to the other scenarios is the need to use polymer in the dehydration phase, whose production process implies a high consumption of this natural resource. However, it is important to note that this scenario stands out for its water recovery capacity, reaching a value of 100 % for the "reclaimed water" indicator, higher than the other scenarios. In the case of S02, a greater recovery of the chemicals used in the process is promoted, evaluated by the "recycled chemicals" indicator, amounting to 80 %, while in the case of S01, the recovery of this polymer after the dehydration stage is not considered, thus becoming an "extra" component in the fertilizer obtained, as well as a significant loss of economic benefit. Similarly, in case S03, there was no recovery of chemicals, even though different chemical agents were used, namely HCl, NaClO₂ or KOH, which also gives a score of 0 for the above indicator. On the other hand, it is worth mentioning that this S03 scenario is also the one with the highest value for the "amount of chemicals" required in the process

compared to the other scenarios, so recycling and valorization strategies should be proposed to increase the sustainable and circular potential of the proposed process scheme.

As a general conclusion it can be stated that (1) it is necessary to assess each indicator separately to identify possible improvement actions, (2) an overall assessment is necessary to identify the potential of the scenario towards sustainable and circular models and (3) it is important to take into account what each indicator represents (i.e. pay attention to its units of measurement) in order to effectively analyze what it refers to. Finally, it could also be concluded that indicators are useful both when the process is in the process design phase, to identify possible improvements prior to the production phase, but even more so when the process is under development, as they could be effective in improving the productivity, sustainability and circularity of the process.

4.7. The role of Green Chemistry principles in the assessment of biorefineries

The consideration of Green Chemistry principles in the assessment of biorefineries in the early stages could be considered as an effective strategy to evaluate whether the process is in line with the concept of sustainability. The principles of Green Chemistry are significantly related to most of the key aspects of sustainable development, but also to health and safety issues, which are relevant to be considered to ensure the well-being of workers and society. While LCA or PEF do not take into account process productivity, resource efficiency or the use of renewable energy, the Greenness Grid methodology, based on the 12 Principles of Green Chemistry, has specific equations to measure these issues. In this sense, it could be said that the application of this methodology has a certain impact on the environmental perspective, but also on the social one, considering for example health and safety issues, and on the economic one, since the productivity in the use of materials is evaluated and scored on a range from 0 to 1, where 1 represents an efficient process. It is also linked to the circularity analysis, as it also measures the amount of by-products generated in the process, as well as the amount of waste, which are particular parameters when talking about moving towards the circular economy.

Regarding the analysis of the results, S01 is the one with the highest value of the Green Chemistry Index, close to 11, which identifies it as the closest to the optimum and as the best among the evaluated scenarios (Fig. 4). The reason for this higher score is that S01 is a more productive process compared to S02 and S03, as it not only produces biogas and biohydrogen, i.e. energy products, but also uses the solid surplus for the production of fertilizers that can be used on farms. It is also a safe process because it does not use highly toxic, flammable or explosive chemicals. Some of the reasons why a higher value of the index has not been obtained are due to the fact that no catalyst is used, in order not to

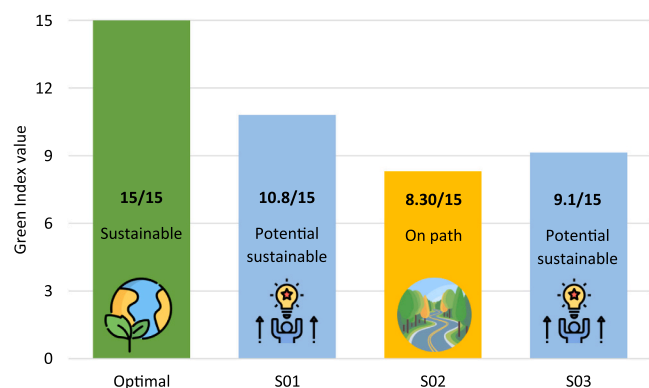


Fig. 4. Green Index values for the S01, S02 and S03.

slow down the process, and in view of the low value of the atom economy, due to the fact that the molecular weight of the chemicals is significantly higher than that of the products, being, among other things, a lignocellulose-based material. These last two conclusions, regarding the use of chemical products and the lignocellulosic nature, are also analogous for scenarios S02 and S03, but the main differences in the values obtained are mainly due to the productivity of the process, the use of resources and energy efficiency. With regard to S03, the value obtained maintains the scenario with the classification of “potential sustainable”, while scenario S02, changes to the classification of “On path”. The effective use of resources is lower in S02 compared to S03, where practically all chickpea shells are used for the production of dietary fiber, thus generating a minimal amount of solid waste. On the other hand, S02 involves several stages and equipment with high consumption, and the energy requirements are significant and not optimized, which implies a reduction in the sustainability potential of the scenario. However, it is important to note that S02 is only 0.70 points away from reaching the same category as the other two scenarios, which

could be achieved by improving the energy efficiency of the process.

5. Combining the essential outcomes of the methodologies into a multidisciplinary assessment framework

A roadmap framework for assessing biorefinery scenarios using different methodologies was developed according to the results of the above analysis and the guidelines of each methodological approach (Fig. 5). Accordingly, the roadmap is based on three main steps, taking into account both sustainability and circularity issues. The first step is based on the development of the Green Index methodology, as it provides a first approximation of the sustainable potential of the scenario. The score obtained from the development of this methodology could range from 0 to 15, with 6 the “cut-off” value, as those scenarios that score below 6 mean that they are unsustainable or critical, and therefore fall far short of what could be considered under the characterization of sustainability. Therefore, the first decision question of the roadmap is: “Is the score below 6?” If the answer is yes, then the scenario needs to be improved (i.e. increase productivity, reduce energy demand, improve product quality, etc.) before it can be assessed using the sustainable and circular methodologies and criteria. On the other hand, if the Green Index is higher than 6, the assessment could continue. The next question to be resolved is the type of scenario to be assessed: if it is a waste treatment process, or if the amount of waste produced compared to the amount of product obtained is higher than 80 %, then the LCA should be developed according to the PEF methodology. On the other hand, if the process developed does not fall within these typologies, then an LCA according to ISO 14040 is recommended. On the other hand, one aspect to consider is the percentage contribution of the waste streams or emissions of the process, since if it is higher than 10 %, then the LCA should also be developed according to the PEF. The reason for this is that the PEF is more recommended as it takes into account the impacts associated with the waste streams and emissions. Once all the sustainable-based assessments are completed, Step 3 of the roadmap is

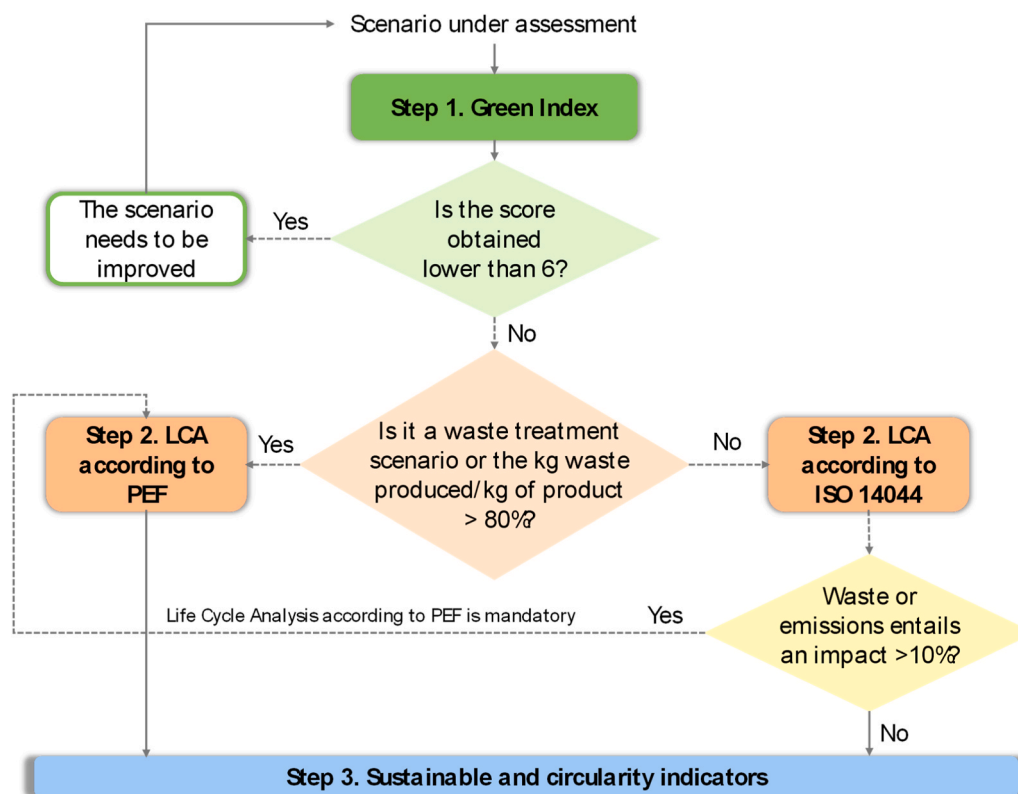


Fig. 5. A multidisciplinary framework for assessing scenarios under a sustainable and circular approach.

developed based on the evaluation of the sustainability and circularity indicators that have been identified as most appropriate to effectively assess the scenario.

To this end, the proposed framework for the evaluation of biorefinery models includes several methodologies, as well as indicators related to sustainability and circularity, considered as an integrated evaluation model in which environmental aspects are evaluated from several perspectives and areas of concern (e.g., climate, waste, energy, water, etc.). First, the use of the Greenness Grid method, centered on the compliance of Green Chemistry principles, integrates several concepts related to productivity, yield, toxicity and efficiency of the process to be evaluated and allows a first global assessment of the sustainable potential of a production model. Secondly, the combination of life cycle analysis methods with the use of indicators provides a more comprehensive view of the weaknesses, vulnerabilities, improvement potentials and strengths of the biorefinery model. The identification of hot spots in the environmental profile and the calculation of indicators facilitate the search for improvements and optimization of biorefinery processes. However, a major limitation in the application of this framework is related to the availability of data to calculate impact factors and indicators. For this reason, although primary data would be ideal to increase the accuracy and veracity of the results obtained, the use of large-scale modeling of biorefinery and biotechnology processes is considered a suitable alternative for the application of the methodologies proposed in the framework.

6. Discussion: Gaps on biorefineries inclusion on value chains, regulatory framework and sustainable aspects of concern

In order to improve the integration of biorefineries into value chains, it is necessary to demonstrate their feasibility, not only in economic terms, but also in relation to technological and environmental performance, which is key to ensure a sustainable bioeconomy [20,68]. One of the main gaps detected is the availability and optimization of feedstocks, in the case of first-generation biorefineries, those based on the use of bio-based materials related to food, the controversy with the food sector is clear so advancing in the use of non-valorized bio-based materials should be enhanced in the near future [46]. The exploration of alternative feedstocks to ensure the viability of biorefineries is a key aspect to be analyzed from the early stages of design, where the development of flexible bio-based production schemes to deal with various biomass sources is considered essential [15].

Another gap identified relates to process efficiency and optimization [44]. In the literature, what can be found is that most of the proposed biorefinery schemes are developed at the laboratory level, thus a very low technological readiness level (TRL), which makes it difficult to assess their potential to be applied at a larger production scale [2]. In addition, most studies are based on the use of emerging technologies, for example, in the case of extraction, the use of ultrasound or deep eutectic solvents, which have not been optimized in depth at higher production levels and could decrease the potential to be applied at a higher TRL. In this regard, addressing scale-up challenges and optimizing the production process are essential aspects to demonstrate the feasibility of bio-based production schemes in “real-world” operating environments [47]. An important aspect to take into account is the fact that the use of bio-based inputs often implies the need to pre-treat biomass to produce high value-added compounds and, depending on the type of technology needed for this step, the impact on economic and environmental aspects could be significant [80]. This could be considered a disadvantage in the use of bio-based resources, so future research should focus on the development of technologies that are efficient and effective, in order to ensure viable costs and proven benefits [31].

To this end, indeed, the integration and development of emerging technologies in the context of biorefineries is considered a good strategy to improve their penetration in value chains, given the expected increase in efficiency and productivity of production schemes given their use (e.

g., the use of genetically modified microorganisms in the fermentation process has shown that it could improve the yield of the process and the quality of the products obtained [18], the consideration of the assisted extraction process could significantly reduce the time required for product extraction while maintaining production yields, thus increasing processing capacity [71], or the use of catalytic conversion technologies, which could increase selectivity and stability [13]). Apart from technological development related to equipment and production schemes, the advancement of technologies for process control and optimization is also important, for example, the integration of machine learning or artificial intelligence, as they could help in the improvement of yields, production capacity and resource efficiency, which are key aspects to ensure the economic and environmental viability of biorefineries and biotechnological processes [5,70].

On the other hand, in order to shape the implementation of biorefineries in the value chains, policies and regulatory frameworks are having a critical role. Governments should work on the inclusion of incentives and subsidies, in the form of, for example, tax credits, tariffs or loans, looking to decrease the non-viability or the risk of not being successful in a long-term [51,59]. Besides, the support of new bio-based projects by policy makers and stakeholders is essential to increase the competitiveness of biorefineries and biotechnological processes in the market. In this aspect, public funding for investigation, research, and development, could accelerate and facilitate bio-based technology transfer in the commercial sector [19,42]. In addition, streamlining regulations and making permitting requirements easier to understand and implement could be useful to reduce burdens on the rapid establishment of biorefineries [54]. Lastly, in order to benefit social communities and workforce growth, governments should also offer programs and training courses in bio-based process and technologies to provide the required skills and expertise for enhancing work opportunities for workers that, at present, are more adapted to the traditional fossil-based models [26,76].

With respect to the environmental sustainability potential of biorefineries, it is expected that the transition to biorefinery models could involve significant environmental benefits compared to traditional fossil-based processes, in which the reduction of emissions causing climate change stands out, mainly related, for example, in the field of biofuel production, such as biodiesel or bioethanol, since they emit lower CO₂ emissions when burned [14]. On the other hand, another outstanding advantage is the use of biorefinery models for the valorization of biowaste, such as waste from the agricultural, industrial, food, sewage treatment plant or municipal sectors, thus reducing the amount of waste that goes to landfills or is directly burned, which has significant negative effects on the environment [78]. In addition, the use of waste as a resource also promotes resource conservation and efficiency, as well as the implementation of circular economy practices [28]. Another important aspect of biorefineries is that they usually have lower emissions of pollutants, such as NO_x, SO₂ or VOCs, compared to current fossil fuel-based systems, which reduces the impact on, in this case, ozone depletion, eutrophication or ecotoxicity, and at the same time improves air and water quality [75].

But, on the other hand, even these potential benefits could be achieved through the penetration of biorefineries, it is necessary to ensure that an efficient use of the related land areas is developed, to avoid trade-offs or unintended consequences (i.e. avoiding indirect land use change, competition with the food sector, or affecting biodiversity protection) [66]. Adequate land use management and planning is required to ensure that there is no risk of deforestation, soil erosion, loss of biodiversity, or to verify that an adequate use of biomass is being developed, seeking to avoid past mistakes made with fossil resources [30,45]. In addition, the implementation of rotational crops in the agricultural and forestry sectors, for large production levels, is considered beneficial to reduce the risk of yield reduction and alteration of ecosystem dynamics, such as natural nitrogen and phosphorus cycles [12,84].

Another aspect to consider is how the transition of biorefineries could have an effect on social communities, as it is also a pillar on the sustainability and circularity approaches. Although most of the implications on social communities could be considered beneficial, biorefineries also involves displacement of vacant jobs in fossil fuel-based industries, requiring relocation to the bio-based sector [86]. In addition, traditional production processes are different from bio-based ones, so workers will also need training to adapt to the new production models, which could be a challenge for them [82]. But apart from this shift, the integration of biorefineries is expected to create more employment opportunities for biomass-related sectors, including the primary and secondary sectors, would involve rural development, as well as economic diversification for, for example, farmers and landowners, helping to improve the quality of life in rural areas [29]. In addition, biorefinery projects could also involve environmental and health benefits, by being more aware of emissions and pollution, such as greenhouse gases or the release of toxic substances, thus improving air quality and resilience to climate change, thus benefiting society as a whole [33].

Regarding the economic dimension, the development of biorefineries could enhance the diversification of markets and regions, where the agricultural and forestry sectors and communities could have emerging opportunities in value chains, thus promoting economic growth in rural areas. The need for biomass feedstocks will imply income for local farmers and landowners, providing more inclusive and equitable economic growth in local communities [58]. The integration of social communities in decision making, as well as the engagement of stakeholders, is considered to have a positive and effective effect on social structures, always ensuring a transparent, participatory and inclusive discussion environment [49].

Finally, another potential benefit is related to stakeholder and community collaboration and engagement, sustainable bio-based projects must be conscious of social welfare and take into account the views and concerns of communities [57]. It is believed that the involvement of society in the decision-making process for the establishment of biorefineries will improve and enhance social equity and well-being [50, 67]. On the other hand, in order to promote social sustainability and prosperity, it is important that new biorefinery models promote social cohesion and respect for communities, as well as concern for social welfare [62]. In this sense, in order to manage all the effects and impacts of the new models, thinking about constant process monitoring and certification with well-recognized certification schemes and ecolabels, which are deeply concerned with ensuring environmental, social and economic sustainability, could be considered as an effective action to be taken [64].

7. Conclusions

In this manuscript, different methodologies and frameworks have been evaluated to identify their potentials, gaps and benefits in the assessment of bio-based process scenarios. The main objective was to provide a critical assessment as well as a multidisciplinary framework to identify the sustainable and circular performance of conventional and bio-based scenarios. Based on the results obtained for the case studies selected for the assessment, the use of PEF for environmental analysis, in contrast to LCA, appears to be limited where there is a clear involvement of the industrial sector with on-site data collection. In the case of the valorization of apple pomace and grape must, the percentage results of the LCA are lower compared to the PEF for almost all impact categories, with the largest differences global warming, freshwater ecotoxicity, fossil resources scarcity, terrestrial acidification, marine eutrophication, human non-carcinogenic toxicity and mineral resources scarcity. In contrast, the LCA methodology gives more relative importance to the human carcinogenic toxicity, ionization radiation and stratospheric ozone depletion. As for GCPs, the assessment of emerging bio-based processes taking into account the principles of green chemistry offers the advantage of assessing whether the production scheme is in line with

the pillars of sustainability, focusing not only on environmental impacts but also on the use of hazardous substances, improving resource efficiency and promoting the use of renewable materials for energy production. The adoption of green chemistry is expected to provide more eco-efficient processes and products and could be seen as a strategy to promote long-term sustainability, resilience and process innovation. The results obtained in the assessed scenarios could be considered in line with the results obtained by the LCA and PEF methodologies, as well as the results obtained by the selected indicators of the certification schemes related to the assessed processes. These indicators are considered to provide a comprehensive approach to assessing the performance of the assessed processes, providing qualitative values and making it easy to identify the main aspects to be improved in order to increase the sustainable and circular potential of the processes. They can also be used as a benchmark for decision making and for promoting continuous improvement of the processes.

To this end, the results and the multidisciplinary framework provided by this manuscript could be considered as a guide for stakeholders, industry leaders, policy makers and researchers on where to focus and how to assess the sustainability and circularity of both established and new emerging industrial processes, including traditional and bio-based ones, promoting innovation, efficiency and liability.

CRedit authorship contribution statement

Gumersindo Feijoo: Writing – review & editing, Supervision. **Ricardo Rebolledo-Leiva:** Writing – review & editing, Investigation. **María Teresa Moreira:** Writing – review & editing, Supervision. **Sara González-García:** Writing – review & editing, Supervision. **Sofía Estévez-Rivadulla:** Writing – review & editing, Investigation, Formal analysis. **Ana Arias:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2024.113361](https://doi.org/10.1016/j.jece.2024.113361).

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