



Offsetting the environmental impacts of single or multi-product biorefineries from wheat straw

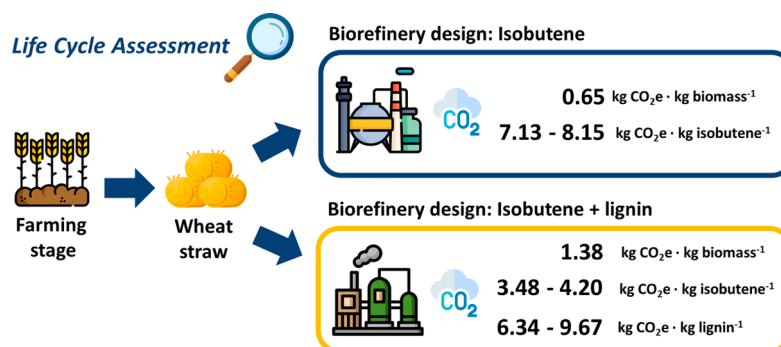
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HIGHLIGHTS

- Midpoint and endpoint environmental profiles for bio-based isobutene are performed.
- Pre-treatment represents the largest environmental burden due to steam demand.
- From a system approach, co-produce lignin increases the impacts of the biorefinery.
- In a product point view, the isobutene profile benefits sharing impacts with lignin.
- Allocation method is a relevant decision to declare an environmental profile product.

GRAPHICAL ABSTRACT



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ABSTRACT

Moving toward a bioeconomy system is fundamental to climate change mitigation, nevertheless, the biotechnological routes should guarantee an environmental sustainability. Isobutene, a precursor in several industrial applications, is one of those chemicals that the environmental effects of its bio-based production have been scarcely explored. This study aims to assess the environmental performance of two biorefinery systems: the first one focuses only on the production of isobutene (I) and the second one on the co-production with lignin (I + L), both from the valorisation of wheat straw. The Life Cycle Assessment methodology is used to determine the environmental impacts considering mid-point and end-point categories. Biorefineries report 0.65 and 1.32 kg CO₂-eq per kg of biomass processed for I and I + L system, respectively. The most affected endpoint damage category corresponds to Human Health, regardless of the scenarios. Moreover, the pre-treatment stage constitutes the main hotspot of both systems considering midpoint and endpoint perspectives.

1. Introduction

Wheat is the most cultivated crop in the world (Le Gouis et al., 2020), due to its vital role in food security (Erice et al., 2019). A challenge in the

management of wheat crops is related to the final use of biomass after harvest. Li and Chen (2020) estimated that 354 Mt of wheat straw is produced each year worldwide. Cereal straw has different end-life uses regarding market or agronomic aims. Thus, the straw can be sold as feed

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(grazing and hay) or as bedding for livestock; otherwise, straw can be left in the field after harvesting for soil amendment or burned to reduce pests and weeds in the next crop cycle (Giannoccaro et al., 2017). In this sense, end-of-life practices are mainly influenced by policy incentives, being soil health a relevant factor of the European Union Common Agricultural Policy (Giannoccaro et al., 2017). In the European context, it is estimated that 58.3 million tonnes of wheat crop residues will be produced by 2030 (Hýšková et al., 2020), showing a broad availability of this resource for its use. Moreover, the interest of using wheat straw on biotechnology production processes is based on its large amount of carbon content (Ginni et al., 2021). It contains a high content of cellulose (28–39 %) and hemicellulose (23–24 %) (Tufail et al., 2021), representing a great fermentable sugars source.

The transition towards a bioeconomy approach in which fossil-based products and energy are replaced by bio-based ones plays a major role in the climate change mitigation strategy. However, it is relevant to assess whether the bioeconomy model is unequivocally linked to sustainable development (Bugge et al., 2016), bearing in mind that the possibility of overexploitation of bio-based resources and arable land is a major concern (van der Ven et al., 2018; Vance et al., 2022).

Analogous to the fossil counterpart, biorefineries allow to obtain multiple co-products based on one or more biomass feedstocks (Julio et al., 2017). In this way, it is possible to co-produce hydrocarbon fuels and high-value bio-based chemicals, improving biomass utilisation efficiency and the economic viability of biorefineries. Therefore, by avoiding dependence on fossil resource consumption, the biorefinery approach appears to be a great potential advantage for reducing greenhouse gas (GHG) emissions, maximising natural resource utilisation and food security (Duan et al., 2020; Yadav et al., 2020). From the biorefinery concept, it is possible to find single-product biorefinery, which focus on the production of one major product, and multi-product biorefinery that obtains different products from the fractions of polysaccharides and lignin, through multiple processes of fractionation, conversion, purification, recovery, among others (Clark and Deswarte, 2015; Clauser et al., 2021), making these systems more economic feasible and efficient through the valorisation of side-flows (Kumar et al., 2020; Obydenkova et al., 2022). However, the widespread confidence that biotechnological process and bio-based products are always a better environmental pathway than fossil-based products require further analysis. The life cycle assessment (LCA) methodology allows understanding the environmental burdens of products or services throughout their entire life cycle (ISO, 2006a). In addition, different impact categories less popular than climate change, such as eutrophication, toxicity, acidification, or land use, can be analysed through this tool, identifying possible trade-offs among them, once the biorefinery system design is under evaluation.

Isobutene (2-Methylpropene) is a highly reactive and small volatile alkene, which represents a relevant feedstock to obtain multiple products such as alkylate gasoline, butyl rubber and specialty chemicals (Mustila et al., 2021). It is expected that the global isobutene market size reach USD 30.71 billion, with demand projected to exceed 16 million tons by 2024 (Grand View Research, 2016). Nowadays, isobutene is manufactured almost entirely from fossil sources through petrochemical cracking of crude oil (Mustila et al., 2021; Van Leeuwen et al., 2012). Therefore, the biotechnological production of isobutene to address the global climate crisis is essential. From the literature, only the study performed by (Lopes et al., 2019) has addressed the mid-point LCA environmental assessment of small-scale biorefineries for isobutene and xylo-oligosaccharides (XOS) production, meanwhile, the lignin stream after enzymatic hydrolysis is combusted.

Traditionally, lignin has been burned as a source of process heat, however, the development of competitive biorefinery system requires adding value to lignin beyond process heat (Davis et al., 2016). Furthermore, literature studies on lignin valorisation describe mainly stand-alone processes and the integration of this route for application in industrial processes, considering the environmental aspects, has been

scarcely addressed (Poveda-Giraldo et al., 2021). In this study, the environmental assessment approach of the wheat straw valorisation into isobutene under a biorefinery strategy considers not only the production of isobutene as the main product, but also the lignin recovery from the solid residue after enzymatic hydrolysis process. Hence, the aim of this work is to determine the environmental feasibility, at early stage of design, of proposing a single-product isobutene and the multi-product isobutene and lignin biorefineries. The above to identify the environmental effects of introducing a lignin recovery route during the biorefinery design. As well as, to determine potential changes in the environmental profile of the main product in both types of biorefineries for an environmental product declaration. Finally, both mid-point impacts and end-point damage categories have been considered for a wider environmental perspective of the potential impacts and damages produced by these systems.

2. Materials and methods

LCA is a comprehensive methodology for assessing the potential environmental impacts of product or service systems throughout their entire life cycle (ISO, 2006a). This method has been widely employed for biorefinery platforms at different scales in recent years (Bello et al., 2018; Câmara-Salim et al., 2021; Rebolledo-Leiva et al., 2022; Santiago et al., 2022). The main goal of this LCA study is provide new information related to the life-cycle environmental impacts of the bio-based isobutene and lignin process in order to justify the possibility of recovery and valorisation of this type of waste from a bioeconomy perspective.

2.1. Systems description

This study follows the LCA methodology according to the ISO 14,040 and 14,044 guidelines for assessing the environmental profile of isobutene and lignin co-production (ISO, 2006a;b). A cradle-to-gate approach is followed, i.e., those production processes from wheat cultivation and the extraction of raw materials to the final production at biorefinery gate. The functional unit (FU) corresponds to 1 kg of wheat straw processed in the biorefinery. Wheat cultivation takes place in Puglia, Italy, therefore, it was assumed that the biorefinery plant is located close to the feedstock supply (Sandén and Pettersson, 2014). In this way, the transport of wheat straw to the biorefinery platform was disregarded (Câmara-Salim et al., 2021).

The design of two biorefinery systems is analysed, in the first system (Scenario I), the focus is on isobutene production, therefore, the system consists of four sections: pre-treatment, enzymatic hydrolysis, fermentation, and recovery. In addition, a waste treatment system is also considered, where biomass is recovered to produce electricity and steam to supply the biorefinery (Fig. 1a). In the second biorefinery system (Scenario I + L), after the enzymatic hydrolysis, a lignin-rich solid flow is obtained, thus, the lignin recovery route is added to the system (Fig. 1b).

2.1.1. Wheat cultivation system

Durum wheat (*Triticum durum*) is grown on an area of approximately 0.25 ha in a monoculture system. Cultivation begins in August with soil preparation and ends in June with harvesting. The main outputs of this stage correspond to wheat grain (13 % moisture) and straw (10 % moisture) with yields of 5.5 and 3.5 t·ha⁻¹, respectively. The market price for wheat grain is 0.29 €·kg⁻¹ and 0.07 €·kg⁻¹ for the straw.

2.1.2. Isobutene production system

To simulate the isobutene production system, the Superpro designer® v11 software was used (see Supplementary Materials). According to Giannoccaro et al. (2017), about 130 kt of wheat straw, representing 30 % of the total annual wheat straw production of the area, is used to feed a combustion power plant in the province of Foggia, in the Puglia Region (Italy). Thus, a biorefinery platform with a capacity

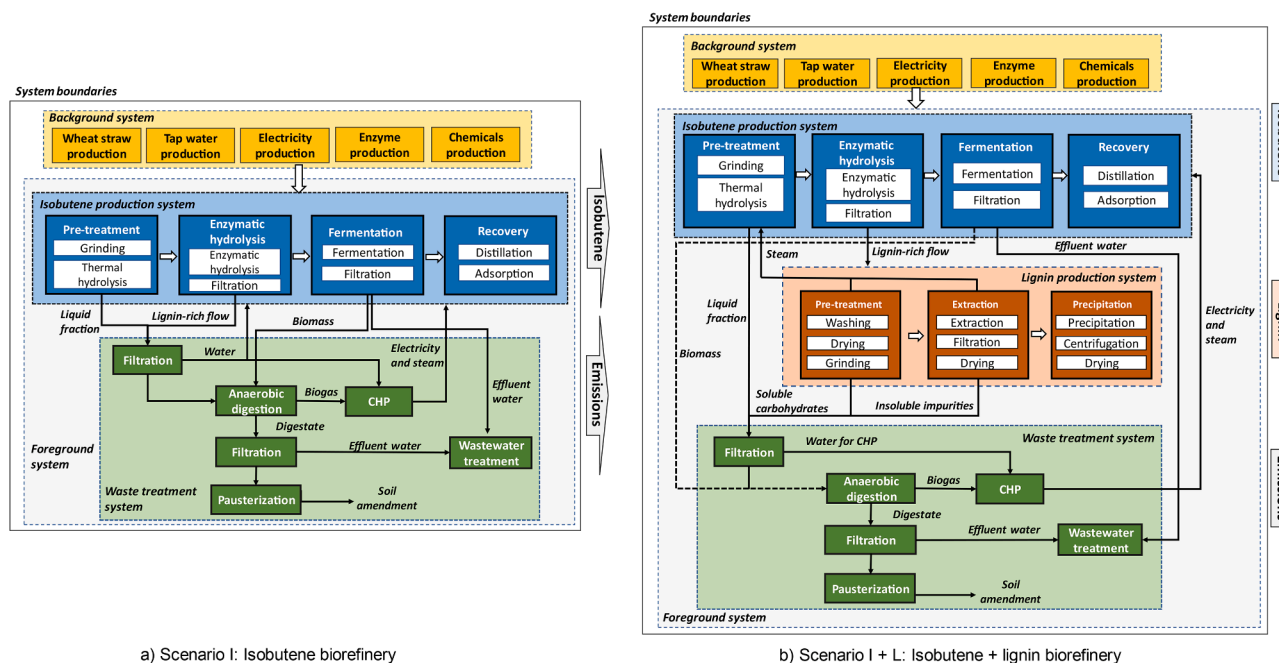


Fig. 1. System boundaries of biorefineries evaluated.

of 45 kt-yr⁻¹ of wheat straw (8,640 h-yr⁻¹) was considered for the process modelling, representing about 10 % of the total annual area with available potential.

2.1.2.1. Pre-treatment section. The straw is shredded to homogenize the straw into particles of 6 mm at 20 °C. The composition of wheat straw expressed in % dry matter is the following: cellulose 38.9 %, hemicellulose 23.5 %, lignin 18 %, ash 9.7 %, protein 4.5 %, and other 5.5 % (Carvalho et al., 2009). The milled straw is sent to an autohydrolysis process to fractionate the conversion of cellulose and hemicellulose. The process is performed at 13 bar and 198 °C (Qiu and Chen, 2012) considering a water-biomass ratio of 2:1 (Al-Zuhair et al., 2013). A fraction of the steam obtained (50 %) from the flash-tank is recovered in this process. Then, a filtration process is applied to separate the solid and liquid fractions. The former goes to the enzymatic hydrolysis section, while the latter goes to ultrafiltration to recover the process water and send it back to autohydrolysis.

2.1.2.2. Enzymatic hydrolysis. The enzymatic hydrolysis is performed using 20 mg·g⁻¹ of Cellic® CTec3 cellulase (Novozymes, Denmark) at 20 %wt of the total solid loading, with a temperature of 50 °C, considering a time residence of 72 h (Lopes et al., 2019). After this step, a filtration process is performed to separate lignin-rich solid stream. This stream goes to ultrafiltration to recover the process water, and then, it is sent to solid waste management in Scenario I, and to the lignin recovery process in Scenario I + L.

2.1.2.3. Fermentation section. A 10 % of the hydrolysate flow is used for microbial growth. This process is performed using a modified *E. coli* strain (Lopes et al., 2019). Nutrients are added and the culture medium is sterilised at 121 °C. Then, the temperature is reduced to 32 °C for the fermentation process. The fermentation time considered is 70 h (Bockrath, 2015). From this process, fractions of approximately 2/3 CO₂ and 1/3 isobutene are obtained in the off-gas stream (Van Leeuwen et al., 2012).

2.1.2.4. Recovery section. In addition to the presence of CO₂ and isobutene presence in the off-gas stream, this gas flow is saturated by water (Van Leeuwen et al., 2012). Therefore, a stage-wise condensation

performance is considered. In this way, a flash condensation is used to condense water, which might contain a certain low percentage of isobutene, which is acceptable as product loss. Therefore, a loss of about 1 % isobutene in this stream was assumed. To obtain a purer product stream, a continuous cryogenic distillation is considered. In this process, the column is operated at 12 bar and the condenser at -19 °C, using CaCl₂ brine as cooling agent. The isobutene obtained from the bottom of the column reaches a purity of 90 %. Therefore, to separate isobutene from CO₂, a granular activated carbon (GAC) adsorption process is considered to increase the purity of the product to 99.6 %.

2.1.3. Lignin recovery system

After enzymatic hydrolysis, a lignin-rich stream is obtained. In Scenario I + L, the design process for lignin recovery is simulated following the procedure proposed by Lo et al. (2021). Briefly, the process can be summarized in three sections:

- i) **Lignin pre-treatment:** The lignin-solid stream is washed with distilled water to remove remaining water-soluble carbohydrates. It is then dried at 105 °C to remove water sampling. The dried biomass is ground and stored at ambient temperature (20 °C) before use.
- ii) **Lignin extraction:** The dried flow is mixed with soda solution (5 % wt NaOH solution) at 190 °C for 300 min. The solution is then filtered to remove insoluble impurities and dried to obtain the solid lignin crude product.
- iii) **Precipitation:** The purity of lignin is further improved by acid precipitation. Most of the lignin in solution would precipitate and can be collected by the centrifugation process. Finally, the stream is dried in a vacuum oven at 105 °C to obtain the final solid product. According to Lo et al. (2021), the final purity of the product is about 71.7 % of insoluble lignin, 5.3 % of soluble lignin and 2.8 % of ash.

The steam obtained from drying processes, in the pre-treatment and extraction lignin stages, is recovered and its pressure is increased (13 bar) to be sent to the pre-treatment section of wheat straw; aiming to supply high-pressure steam for the thermal hydrolysis.

2.1.4. Waste management system

Different waste flows are obtained from the production sections in both scenarios. In Scenario I, the liquid flow from the pre-treatment, the lignin-rich stream and the biomass from the fermentation are sent to the anaerobic digestion (AD) process to produce biogas (see Fig. 1a). In Scenario I + L, the waste streams sent to the AD process correspond to those obtained from the pre-treatment and fermentation processes in isobutene production, as well as those obtained from the pre-treatment and lignin extraction processes (see Fig. 1b). The digester operates at atmospheric pressure (1 bar) at 32 °C with a residence time of 30 days (Lopes et al., 2019). The biogas obtained is fed to a gas turbine-generator and a steam generator to produce power and heat. An electrical conversion efficiency of 32 % and a heat recovery potential of 53 % is assumed (Banks et al., 2011). The steam production is mainly focused to obtain high-pressure steam (13 bar) to meet the heating demands of the thermal hydrolysis stage in the pre-treatment section. A little fraction (2 %) of low-pressure steam obtained (5 bar) supplies other heating requirements in the same section. The generated electricity is added to the biorefinery platform to reduce its energy demand to the grid, mainly related to the pre-treatment section. In addition, 10 % of the digestate is returned to the AD process, while the non-recycled digestate is dewatered through centrifugation. The liquid fraction obtained is sent to the wastewater treatment plant. The dewatered digestate is pasteurised at 70 °C for 1 h (Santiago et al., 2022), then transferred to a storage tank, until it is used as a soil amendment. In this sense, 16 % of the carbon content of the biomass will be stored in the soil as soil organic carbon in the long term (Fang et al., 2019), considering a carbon content of about 35 % of its dry matter.

2.2. Life cycle inventory

The wheat crop inventory data is summarised in Table 1, which was collected through surveys with farmers located in Apulia, Italy. To allocate the environmental burdens between grain and straw, an economic allocation method was assumed, considering a load distribution of 85.5 % for grain and 14.5 % for straw. In addition, inventory data for the isobutene and lignin production systems were obtained by means of mass and energy balances modelled in the Superpro designer® v11 software (see Supplementary Materials). In Scenario I + L, where two products are obtained, a mass allocation approach is used to assign the environmental burdens. Regarding the background processes associated to raw material production, the Ecoinvent® v3.8 database (Wernet et al., 2016) was used, through the Simapro v9.3.0.2 software (PRÉ Consultants, 2020).

2.3. Life cycle impact assessment

To assess the environmental burdens of biorefinery platforms, two Life Cycle Impact Assessment (LCIA) methods were considered: the ReCiPe 2016 Midpoint (H) V1.06 / World (2010) (H) and the ReCiPe

Table 1
Inventory data corresponding to the wheat straw cultivation stage.

Life Cycle Inventory data	Value	Unit
Nitrogen application, as N	104.4	kg·ha ⁻¹
Phosphorus application, as P	40.2	kg·ha ⁻¹
Pesticides application (active ingredient)	2.0	kg·ha ⁻¹
Seed	180.0	kg·ha ⁻¹
Diesel	42.3	l·ha ⁻¹
<i>Field emissions</i>		
N ₂ O	1.64	kg·ha ⁻¹
NO ₂	4.18	kg·ha ⁻¹
NH ₃	2.96	kg·ha ⁻¹
N O ₃ ⁻ leaching	114.6	kg·ha ⁻¹
P—P O ₄ ³⁻ leaching	70	g·ha ⁻¹
P—P O ₄ ³⁻ runoff	220.0	g·ha ⁻¹

2016 Endpoint (H) v1.06/ World (2010) H/A (Huijbregts et al., 2017). The first one is employed to obtain the characterization impact values and the second one to compare single score values at the development stage of design. Regarding the endpoint approach, the selected (H/A) World (2010) version is the default method and uses a hierarchist (H) perspective, average (A) weighting set, and global normalization factors for the reference year 2010 (Herrando et al., 2022). In the midpoint perspective, the environmental impact categories analysed correspond to Global Warming - GW (kg CO₂·eq); Particulate Matter - PM (kg PM_{2.5} eq); Terrestrial acidification - TA (kg SO₂ eq); Freshwater Eutrophication - FE (kg P eq); Marine Eutrophication - ME (kg N eq); Human Carcinogenic Toxicity - HT (kg 1,4-DCB); Land Use - LU (m²a crop eq); Fossil Resource Scarcity - FRS (kg oil eq). Concerning the endpoint approach, the damage categories analysed are: Human Health, Ecosystem Quality and Resource Scarcity.

3. Results and discussion

3.1. Environmental impacts analysis: Midpoint perspective

The overall mid-point environmental impacts of the biorefinery system according to both scenarios evaluated are presented in Table 2. Regarding the Scenario I, the pre-treatment section is the stage that contributes the most to the environmental impacts of bio-based isobutene production in almost all categories (see Fig. 2a), with a range value of 33 % to 73 % in FE and ME categories, respectively. Meanwhile, the enzymatic hydrolysis section is the main contributor in the LU category, due to enzyme production. The contribution of the unit processes in each section is presented in the Supplementary Materials. Concerning the Scenario I + L, the lignin recovery route is the main contributor in all impact categories, with a range value of 54 % to 78 % in LU and FRS categories, respectively (see Fig. 2b). In the lignin production, the extraction process is the main hotspot in six categories such as GW, PM, TA, FE, HT, and FRS (see Fig. 2d). In addition, the pre-treatment of wheat straw and the enzymatic hydrolysis are the main contributors in ME and LU categories, respectively. The first one due to the wheat straw production, and the second one due to enzyme fabrication. Regarding the isobutene product in the I + L system, the recovery stage appears as the hotspot in GW, PM, TA, FE, and HT categories (see Fig. 2c). Furthermore, the pre-treatment, enzymatic hydrolysis and fermentation stages are the processes of concern in ME, LU, and FRS categories, due to wheat straw, enzyme, and nutrient production, respectively. Accordingly, these results show changes between both biorefinery designs, based on the relevance of the processes to the environmental profile. The reason behind this is due to the steam supply from the lignin valorisation route to the pre-treatment stage of the wheat straw, specifically to the thermal hydrolysis, which leads to lower demand for this resource, and consequently, an improvement in the environmental declaration of isobutene product. Hence, the potential synergies among valorisation routes (i.e., side-flows recovery to reduce resource consumption in elaboration of the main product) during the biorefinery design allow benefiting the environmental declaration of the products obtained, particularly to the main product of interest. The main results for both biorefineries according to each impact category are described below.

3.1.1. Global warming

In Scenario I, the pre-treatment section is the main contributor with about 56 % of the total, due to the energy requirement of thermal hydrolysis process, i.e., high-pressure steam. This hydrolysis process accounts for about 78 % of the CO₂·eq emissions related to the biomass pre-treatment stage. The remaining 22 % corresponds to the grinding process (see Supplementary Materials). The second largest contributor to this impact category is the recovery section with about 17 %, due to the energy requirement in the distillation process. The fermentation stage represents approximately 14 % of the CO₂·eq emissions. The GHG

Table 2
Mid-point and end-point environmental profiles for both scenarios (FU: 1 kg wheat straw processed).

Midpoint perspective								
Impact category	Unit	Scenario I	Scenario I + L					
			Isobutene	Lignin	Total			
GW	kg CO ₂ eq	0.648	0.334	1.049	1.382			
PM	g PM _{2.5} eq	0.867	0.506	1.173	1.679			
TA	g SO ₂ eq	2.815	1.555	3.29	4.845			
FE	g P eq	0.218	0.136	0.284	0.42			
ME	g N eq	0.457	0.21	0.263	0.474			
HT	kg 1,4-DCB	0.011	0.007	0.016	0.023			
LU	m ² a crop eq	0.077	0.038	0.046	0.085			
FRS	kg oil eq	0.215	0.101	0.348	0.449			

Endpoint perspective								
Damage category	Scenario I					Scenario I + L		
	Pre-treatment	Enzymatic hydrolysis	Fermentation	Recovery	Total	Isobutene	Lignin	Total
Human health	15.4	3.99	3.94	4.83	27.3	14.2	40.5	54.7
Ecosystems	0.94	0.27	0.27	0.15	1.51	0.73	2.1	2.84
Resources	0.31	0.05	0.05	0.04	0.5	0.21	0.81	1.03
Single score	16.6	4.26	3.02	5.03	29.3	15.2	43.4	58.6

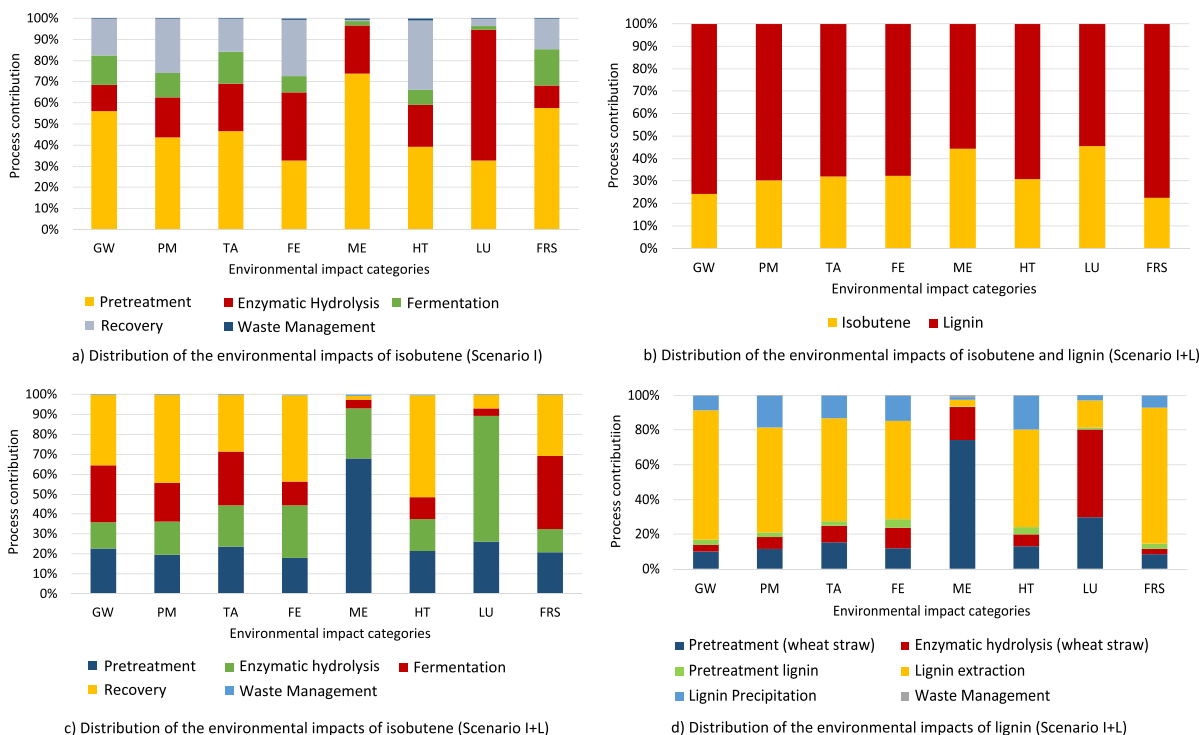


Fig. 2. Distribution of the environmental burdens in Scenario I and Scenario I + L.

emissions in Scenario I are distributed as follows: 85 % for CO₂ fossil, 8 % for N₂O, and 6 % for CH₄. The CO₂ fossil emissions occur mainly in the pre-treatment section (56 %), due to heat production. In Scenario I + L, the lignin production is about 76 % of the CO₂.eq emissions (see Fig. 2b), being the extraction process the main contributor with about 75 % of the CO₂.eq emissions (see Fig. 2d) due to the steam demand. The GHG emissions in Scenario I + L are distributed as follows: 89 % for CO₂ fossil, 7 % for CH₄, and 4 % for N₂O. CH₄ and N₂O emissions occurs mainly in the lignin production with about 65 % and 52 %, respectively.

3.1.2. Particulate matter

In Scenario I, the pre-treatment section is the main hotspot with

about 44 % of the PM_{2.5}.eq emissions, due to energy requirement for the thermal hydrolysis process (about 60 % of the pre-treatment section). The recovery and enzymatic hydrolysis sections account for approximately 25 % and 19 % of particulate emissions, respectively. This is due to the distillation process in the former and enzyme production in the latter. In terms of emission contribution, sulphur dioxide (SO₂) is the main load with about 48 %, followed by particulate matter <2.5 μm with about 22 %. In Scenario I + L, the lignin accounts for 70 % of the total emissions. In lignin production, the extraction and precipitation processes account for 60 % and 18 % of the impacts, due to heat and hydrochloric acid requirements, respectively. In this scenario, SO₂ accounts for 53 % of the emissions, followed by particulate matter <2.5

μm with 25 % of the total. Lignin makes 75 % of the contribution to SO_2 emissions and 67 % to particulate matter $<2.5 \mu\text{m}$.

3.1.3. Terrestrial acidification

In Scenario I, the pre-treatment section is the main contributor with about 47 % of $\text{SO}_2\text{-eq}$, due to steam production (about 52 % of the pre-treatment section). Enzymatic hydrolysis is the second largest contributor with 23 % of the impacts, due to enzyme production (90 %). SO_2 is the main emission with about 51 %, followed by ammonia (NH_3) and nitrogen oxide (NO_x) with 32 % and 15 %, respectively. In Scenario I + L, lignin accounts for about 68 % of the total impacts, with the extraction process as the concern process with 60 % of the $\text{SO}_2\text{-eq}$ impacts, followed by biomass pre-treatment with 15 %. In this scenario, SO_2 emissions represent 63 %, followed by NH_3 with 19 %, and NO_x with 16 %.

3.1.4. Eutrophication categories

In Scenario I, in FE category, the contribution of the processes is quite equilibrated, the pre-treatment and the enzymatic hydrolysis account for about 33 % and 32 % of the total, respectively, while the recovery section represents about 26 % of the overall impacts. This occurs due to the steam, enzyme, and cooling agent requirements. Phosphate emissions represent about 71 %, followed by phosphorus (water) with 12 % and COD (Chemical Oxygen Demand) with 11 %. Regarding ME category, pre-treatment represents about 74 % of the total due to wheat straw production. Moreover, nitrate (NO_3^-) is the main contributing emission with about 97 %. In Scenario I + L, in the FE category, the lignin product accounts for about 68 % of the impacts, mainly, because of the biomass pre-treatment (wheat straw cultivation). Phosphate is the main emission with 80 % of the impacts. Meanwhile, in the ME category, the contribution of both bioproducts are closer: lignin with 56 % and isobutene with 44 %. In the lignin product, biomass pre-treatment is the main concern of the impacts (due to wheat straw cultivation). Moreover, NO_3^- is the main pollution factor with 96 %.

3.1.5. Human carcinogenic toxicity

In Scenario I, the pre-treatment represents about 39 % of the impacts, followed by recovery and enzymatic hydrolysis with 33 % and 20 %, respectively. In the pre-treatment section, wheat straw cultivation is the main reason for the impacts (53 %). Meanwhile, the distillation process is behind the impacts of the recovery section, due to the cooling agent requirement. Similarly, enzyme production is responsible for the contribution of the enzymatic hydrolysis. As indirect emissions in the life-cycle isobutene production, Chromium VI is the main emission in this category with about 90 %, followed far by Arsenic with 3 %. Both are highlighted in the pre-treatment and recovery sections. In Scenario I + L, lignin represents about 69 % of the total, where the extraction is the main responsible of the burdens due to steam requirement (52 % of the impacts in this stage). Furthermore, the recovery process accounts for 52 % of the overall impacts in the isobutene production. In this scenario, 90 % of the emissions are based on Chromium VI, mainly from lignin production (69 %).

3.1.6. Land use

In Scenario I, enzymatic hydrolysis is the main contributor with about 62 % of the impacts, followed by pre-treatment with 33 %. The main reason behind this is the demand for enzyme and wheat straw, respectively. In Scenario I + L, both products contribute with almost equal importance: 54 % for lignin and 46 % for isobutene. Enzymatic hydrolysis appears as the main contributor in this system, followed by the biomass pre-treatment.

3.1.7. Fossil resource scarcity

In Scenario I, pre-treatment accounts for 58 % of the total impacts, followed by fermentation with 17 %, and recovery with 14 %. As expected, the hydrothermal process is the main contributor of the biomass fractionation (87 %), due to steam production. Meanwhile, in the

fermentation section, nutrients for the growth of culture are the main hotspot. Natural gas is the main raw material consumed with 62 % of the total emissions, followed by oil crude with 19 %. In Scenario I + L, 68 % of the emissions are associated with lignin valorisation. Steam production is the main contributor in the extraction section. Like the Scenario I, natural gas is the raw material responsible for about 60 % of the emissions.

3.2. Environmental impacts analysis: Endpoint perspective

To make a comparison between both biorefinery designs, all impact categories have been quantified in a single score (mPt) covering the three damage categories. As can be observed in Table 2, the potential damages of Scenario I + L are almost twice the amount obtained in scenario I. As well as it is possible to identify that the lignin route valorisation reaches a higher score than the overall Scenario I (43.4 against 29.3 mPt). The relevant concern in both systems is the Human Health category, which represents 93 % of the total score. Regarding the Scenario I, the pre-treatment stage is the most impactful stage of the biorefinery system in all three damage categories assessed. This is mainly due to the need for steam for the thermal hydrolysis treatment. Concerning the Scenario I + L, the potential damages obtained is mainly due to the lignin valorisation, which represents about 74 % of the total. The steam demand in the extraction process appears as the main factor of attention in this route.

3.3. Sensitivity analysis

3.3.1. Economic allocation approach

The impact values obtained were studied considering a mass allocation approach in Scenario I + L. However, in order to identify the robustness and variability of the impact results based on the selection of the allocation procedure, an economic perspective was also considered. Considering a market price of $2017.4 \text{ USD}\cdot\text{t}^{-1}$ for isobutene (Lopes et al., 2019) and $300 \text{ USD}\cdot\text{t}^{-1}$ for lignin (low purity assumption) (Poveda-Giraldo et al., 2021), a distribution of 83.1 % for isobutene and 16.9 % for lignin is obtained. Accordingly, from Table 3, some changes in the distribution of the environmental burdens with respect to the mass allocation. In the economic approach, isobutene production route obtains higher impact values per biomass processed relating to the mass perspective, due to the different allocation factor employed in this measure (42 % in mass allocation) based on the higher economic significance of isobutene product, which is the main purpose of both systems. The increase in the isobutene environmental profile ranges from 18 % to 67 % in FE and ME, respectively.

3.3.2. Product functional unit

Table 3 also presents the environmental impacts from a product perspective, i.e., considering the kg of product as functional unit for both allocation methods. Thus, the environmental profile of isobutene is, as can be expected, higher when the production is only focus on this product (Scenario I). For example, in the GW category, the value obtained in Scenario I is almost twice that of Scenario I + L in the mass allocation approach and 58 % above the profile obtained in the economic allocation. Hence, introducing another valorisation route benefit the environmental declaration of the main product (i.e., isobutene). Other reductions, based on the isobutene profile of Scenario I, that can be highlighted are ME, FRS, and LU with a reduction of about 54 %, 53 % and 51 % respectively, with the Scenario I + L in the mass allocation approach. Meanwhile, in the economic allocation, the isobutene profile obtains reduction of 43 %, 37 %, 32 % in FRS, LU, and TA, respectively. As it is mentioned above, the reason behind the higher impacts in the isobutene profile with the economic allocation is due to the greater allocation factor with respect to mass allocation considering the same production yield.

Table 3

Environmental profiles based on economic and mass allocation and per kg of product.

Environmental profile of Scenario I + L based on economic allocation (FU: 1 kg wheat straw)				
Impact category	Unit	Isobutene	Lignin	Total
GW	kg CO ₂ eq	0.408	0.974	1.382
PM	g PM _{2.5} eq	0.602	1.076	1.679
TA	g SO ₂ eq	1.912	2.933	4.845
FE	g P eq	0.160	0.260	0.420
ME	g N eq	0.350	0.124	0.474
HT	kg 1,4-DCB	0.009	0.014	0.023
LU	m ² a crop eq	0.048	0.036	0.085
FRS	kg oil eq	0.121	0.327	0.449

Environmental profile for both scenarios based on 1 kg of product						
Impact category	Unit	Scenario I	Scenario I + L (Mass-allocation)		Scenario I + L (Economic allocation)	
			Isobutene	Isobutene	Lignin	Isobutene
GW	kg CO ₂ eq	8.15	4.20	9.67	5.13	8.98
PM	g PM _{2.5} eq	10.9	6.36	10.81	7.58	9.92
TA	g SO ₂ eq	35.4	19.56	30.32	24.04	27.04
FE	g P eq	2.74	1.71	2.62	2.01	2.40
ME	g N eq	5.75	2.64	2.43	4.40	1.14
HT	g 1,4-DCB	139	89	147	108	133
LU	m ² a crop eq	0.97	0.48	0.42	0.61	0.33
FRS	kg oil eq	2.7	1.27	3.21	1.53	3.02

3.3.3. Steam improvement

In the previous both Scenarios I and I + L, 70 % of the biogas produced goes to the gas turbine-generator to produce electricity, and the remaining 30 % goes to the steam generator to produce steam. Since steam production is a critical factor in the environmental profile of biorefinery systems in the midpoint and endpoint perspective, 90 % of the biogas obtained is used to produce high-pressure steam to supply the pre-treatment section. Fig. 3 presents the results with this strategy, showing different performances based on the category analysed. In Scenario I (Fig. 3a), the GW and FRS categories were reduced by about 12 % and 14 %, respectively. Meanwhile, a marginal increase of about 7 % is obtained in the FE and HT categories, which exposes the trade-off issue in the definition of improvement strategies, some categories can improve but others can obtain worse results, which is the multicriteria perspective of the impact assessment with the LCA approach. The growth in the impacts occurs due to the increase in electricity demand, which is not compensated by the reduction in steam requirement. In contrast, in the Scenario I + L, all impact categories are reduced with this strategy (see Fig. 3b). This happens because Scenario I + L obtains a significant improvement in the steam production from about 615 kg·h⁻¹ in baseline scenario to 1,845 kg·h⁻¹ with the prioritization of steam production. In the endpoint perspective, the results are very similar in both scenarios.

3.4. Comparison of the results with literature data

For isobutene production based on petrochemical sources, very little data is available due to confidentiality issues and patent rights. One of the main challenging aspects of conducting an LCA study for fossil isobutene or other fossil-based products is to overcome this lack of data. This is a relevant aspect that limits the comparison with bio-based production systems in order to identify quantitatively the benefits of

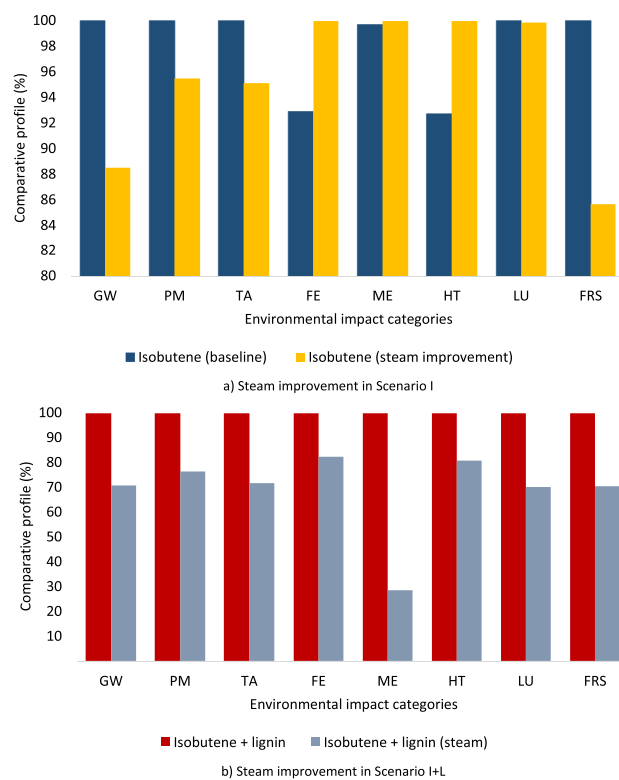


Fig. 3. Comparison of environmental profile focusing on steam recovery.

the bioeconomy approach. In this regard, the first tentative environmental profile of fossil-based isobutene production is provided by the OPTISO-CHEM project (Lassacher et al., 2018). This project report assessed the carbon life cycle analysis of three fossil isobutene routes based on its own estimates through literature data. The environmental impacts were characterised through the CML 2001 method, considering a mass allocation approach. Thus, to compare the environmental profiles, the CML-IA baseline V3.07 / EU25 was used, focusing only in the GW category, since there are still some differences between both LCIA methods. The fossil production routes are: a) from *tert*-butyl alcohol (TBA) dehydration, where TBA is a co-product of propylene oxide production (Oxirane process); b) from Methyl-*tert*-butylether (MTBE) cracking; c) from isobutane dehydrogenation. According to this project report, isobutene is obtained from TBA, which is the coproduct of the propylene oxide production. Thus, two allocations are required: oxirane process (two products, 75 %) and TBA decomposition (three products, 96 %). As well as in this bio-based production, the steam production is the main contributor in GW. In the second route based on MTBE, one allocation is required (61 %) for the three co-products obtained (fuel, methanol, and isobutene), and the lowest isobutene profile is obtained from the three routes (see Table 4). However, if one of the co-products (methanol) would be neglected, the allocation factor would increase to 95 % obtaining a value per kg of product of 3.1–3.6 kg CO₂eq. The last route is obtained from GaBi ts 6.5 professional database (Kupfer

Table 4

Comparison with three fossil-based production per kg isobutene.

Scenarios	GW impact (kg CO ₂ eq)
From <i>tert</i> -butyl alcohol (TBA) dehydration	2.14 – 2.99
From MTBE decomposition	1.92 – 2.36
From isobutane dehydrogenation	2.51
Bio-based isobutene (I)	8.15
Bio-based isobutene (I, steam improvement)	7.13
Bio-based isobutene (I + L)	4.20
Bio-based isobutene (I + L, steam improvement)	3.48

et al., 2017). In this regard, these bio-based production routes obtained higher impact values than the three fossil routes. However, the allocation of the burdens can be the reason behind these differences.

According to the above, the multiple bioproduct perspective can be a key aspect for the comparison of the environmental profiles of a product between valorisation routes. Here, the single product isobutene biorefinery (Scenario I) obtains almost fourth times the GW impact profile with respect to the fossil-based production. Nevertheless, when the design of the biorefinery aims to obtain multiple products (Scenario I + L), the environmental profile of the main product can be improved. Accordingly, in this study, the bio-base isobutene profile was closer to the estimation of the fossil production in Scenario I + L. Hence, it seems not to be fair to compare single and multiple product biorefinery designs, due to the quite relevant role that the allocation of burdens plays in this context. This can be exemplified with the second fossil route production (i.e., the MTBE decomposition), where reducing from three (isobutene, methanol, and fuel) to two products (isobutene and fuel), the environmental profile of isobutene can reach 3.1–3.6 kg CO₂-eq, similar to the biorefinery I + L, which obtains 3.5 kg CO₂-eq in the sensitivity analysis with the steam improvement. Therefore, it is recommended that the comparison of different production or valorisation routes based on fossil or renewable sources should be carefully addressed to avoid harm or benefit the environmental declaration of the product evaluated. Furthermore, since the results obtained by this project are the first approach to the environmental profile of fossil-based isobutene production, further research is required for reliable comparisons. Otherwise, from a system perspective, design a platform to incorporate more valorisation route to obtain the major number of bioproducts possible, implies increasing the overall impacts of the biorefinery per biomass processed. This can be observed from the 0.648 to 1.389 CO₂-eq emissions per wheat straw obtained from Scenario I and Scenario I + L, respectively.

Another bio-based isobutene production is proposed by Lopes et al. (2019), which also co-produce xyloligosaccharides (XOS), and produce electricity from the cogeneration (CHP) system, based on the biogas obtained through the swine manure processed in an AD process. These authors used the ReCiPe method and considering an economic allocation. The results obtained, focusing on GW category, for their biorefinery systems were 0.796 and 0.760 kg CO₂-eq per kg wheat straw for Portugal and Chile, respectively. Their results are like the performance obtained in this study of 0.648 kg CO₂-eq per kg of wheat straw in Scenario I, but lower to the 0.970–1.398 kg CO₂-eq in Scenario I + L. The main reason behind this difference corresponds to the use of swine manure as an extra feedstock to supply the AD process and obtain, in this way, steam and electricity for the biorefinery.

Concerning the environmental profile of the isobutene production, per kg of product, Lopes et al. (2019) obtained a value of 2.72 and 2.19 kg CO₂-eq for Portugal and Chile, respectively. These profiles are lower than the 4.20 and 3.48 kg CO₂-eq obtained in this study, but it is important to consider the differences among these biorefinery designs related to the use of manure, as it was mentioned before. Furthermore, the impacts related to wheat straw/corn stover and manure production were out of the system boundary. In Lopes et al. (2019), the hydrolysis and fermentation section represents the main contributor in the GW category. Moreover, considering manure as another external input for the AD process allowed to obtain a surplus of electricity, which was supposed to be sold to the grid. Consequently, electricity is considered another co-product. In this way, an important characteristic in the environmental profile of this bio-based isobutene is that the economic allocation implies a distribution burden of only about 19 % for this product. Where the XOS products obtain about of 46 % and 44 % of the impacts, due to the market price of the XOS products is twice time the market value of isobutene. In this context, due to the multifunctional nature of biorefineries, the method used to handle allocation is a significant decision for the declaration of the environmental product profiles (Vance et al., 2022).

Other biorefinery studies present similar discussion, for example, Cai et al. (2018) founded that allocation methods could change the resulting life cycle GHG emissions significantly in the co-production of succinic acid or adipic acid. As well as Timonen et al. (2019) concluded that allocation by energy, economic or mass value significantly change environmental burdens in biogas and digestate production from AD processes. The selection of the allocation method should be carefully addressed when the environmental burdens of the biorefinery design are under evaluation. The life-cycle results are highly sensitive when co-products are considered in the process modelling. Product-specific impact profiles can vary significantly with the distribution of the total biorefinery impacts, benefiting differently to the main product and co-products.

4. Conclusions

From a product declaration perspective, in the single product biorefinery, all environmental loads are related to isobutene, obtaining a higher impacts profile than the co-production with lignin, due to burdens allocation. From a biorefinery design approach, incorporating more processes increase the environmental performance of the platform per biomass processed. The limitations of this study were related to the scarce availability of data to compare fossil-based isobutene production with the bio-based route. Moreover, since the steam demand is a critical aspect of the system, strategies are required to optimize its consumption.

5. Data Availability

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its [Supplementary Materials](#).

CRediT authorship contribution statement

Ricardo Rebolledo-Leiva: Conceptualization, Investigation, Methodology, Formal analysis, Software, Visualization, Writing – original draft, Writing – review & editing. **María Teresa Moreira:** Supervision, Writing – review & editing, Visualization. **Sara González-García:** Supervision, Writing – review & editing, Visualization, Funding acquisition.

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. Supplementary data

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