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Identifying the sustainability route of asparagus co-product extraction: From waste to bioactive compounds

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ABSTRACT

Rutin is a flavonol glycoside that is found in greater proportion in asparagus stalks. Considering the possibility of valorization of solid waste from the food industry, this research aims to evaluate and compare the environmental profile of the different schemes of rutin asparagus extraction. Specifically, Soxhlet, pressurized liquid and supercritical fluid extractions, all of them using ethanol as the extracting agent. The environmental analysis is conducted according to the Life Cycle Assessment methodology under a mass and economic allocation. The results, under economic allocation, show that the scenario based on pressurized liquid extraction have the best environmental profile. However, when mass allocation is considered, the pressurized liquid-based scenario is the worst choice. Consequently, the choice of the solvents will influence the Soxhlet extraction performance. In this regard, ethanol, methanol and ethyl acetate are selected. The solvent comparison identifies ethyl acetate as the extraction agent with the worst environmental profile.

1. Introduction

Throughout the food supply chain, food waste is produced at each stage (manufacturing, sale and consumption). Approximately 39% of the food produced is wasted at the manufacturing stage (Cristóbal et al., 2018) due to overproduction or poor appearance for sale. Among the 17 Sustainable Development Goals (SDG) (United Nations, 2015), the most appropriate management of value chains in food production is included in SDG number 12 (Responsible Consumption and Production), which aims, among others, to reduce food loss as well as the implementation of recycling or reuse strategies (United Nations, 2015).

Taking into account the prohibition of the disposal of food waste in landfills according to the Council Directive 2008/98/EC (European Union, 2008), two valorization options arise: either for the production of animal feed (Cristóbal et al., 2018; Drosou et al., 2015) or for the production of bioenergy in anaerobic digestion processes (Cristóbal et al., 2018; Drosou et al., 2015). However, based on the characteristics of the waste, it is possible to develop biorefinery strategies to produce high value-added products with nutraceutical and pharmaceutical applications (Cristóbal et al., 2018). There are several studies available in the literature in which different types of food residues such as horse chestnut burs (Gullón et al., 2020), tomato (Gharbi et al., 2017) and grape pomace (Tournour et al., 2015) are valorized into lignin and glucose, antioxidants and phenolic compounds, respectively.

Asparagus (*Asparagus officinalis* L.) is one of the main stem vegetables grown in Spain (Spanish Ministry of Agriculture, Fisheries and Food, 2020). Its production, at national level, was about 68 thousand tons in 2018, approximately 4% of total cultivated vegetables (Spanish Government, 2020). Spain is the second largest producer of asparagus in Europe, after Germany, cultivating and harvesting more than 21% of total European production (European Commission, 2021). The edible part of the asparagus corresponds to approximately 50%

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of its total, being the other half (inedible part) discarded during processing (Fuentes-Alventosa et al., 2013; Zhao et al., 2011). As for its nutritional quality, asparagus is a good source of phenolic compounds, mainly flavonoids, including rutin (3′,4′,5,7-tetrahydroxy-flavone-3-rutinoside), a flavonol glycoside with an important use in pharmaceutical, cosmetic and food industry due to its antioxidant, anti-inflammatory, antimicrobial, anticancer or antidiabetic properties (Gullón et al., 2017; Solana et al., 2015; Zhang et al., 2018a).

The demand for natural rutin has increased, therefore it is important to assess the alternatives developed for its extraction from plant biomass (Chua, 2013; Gullón et al., 2017; Vangalapati et al., 2015). Extraction techniques range from traditional (e.g. solvent extraction) to advanced techniques (Solana et al., 2015; Vangalapati et al., 2015) such as pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), or ultrasound-assisted extraction (UAE) (Chaves et al., 2020).

These techniques are effective to obtain flavonoids among the various types of natural matrices (Chaves et al., 2020) and are known as "green" techniques in the literature (Chaves et al., 2020; Chemat et al., 2012; Sengar et al., 2020). Among its main advantages are the reduction in the consumption of organic solvents as well as the extraction times. Furthermore, according to (Mondello and Salomone, 2019), a "green process" would allow reducing environmental impacts among all the processes involved in the activities destined to obtaining the product. However, considering that both MAE and UAE present a remarkable complexity when aiming at the scale-up the process from laboratory scale experiments (Li et al., 2013; Vinatoru et al., 2017), the green extraction techniques considered for assessment in the present study will be PLE and SFE.

The choice of solvent is the key variable in any extraction method. In general, organic solvents, water and mixtures of both are commonly used for the extraction of flavonoids from plant matrices (Chaves et al., 2020). In addition, several studies have shown that, due to the polarity of flavonoids (as is the case with rutin), organic solvents, such as ethanol, methanol and ethyl acetate, are more efficient for their extraction (Solana et al., 2015; Vangalapati et al., 2015).

However, depending on the final use of rutin (i.e., food, cosmetic or pharmaceutical production), not all of these solvents can be used interchangeably. In this respect, if rutin is intended for food applications, ethanol would be the best option as an extracting agent, since its use in the food sector is accepted by the European Food Safety Authority (EFSA) (EFSA, 2012) and the European Commission Directive 2016/1855 (European Commission, 2016). Similarly, ethyl acetate is also considered suitable for use as an extraction solvent in the processing of food products (EFSA, 2012; European Commission, 2016). However, methanol is not allowed to be used as an extraction agent in food applications due to its toxicity potential (Muñiz-Mouro et al., 2018). Bearing in mind these considerations and that the rutin extracted in this study is intended to be used in food applications, ethanol is the solvent of choice as an extracting agent. As for the novel techniques mentioned above, it is interesting to know which one is the most recommended from the environmental point of view, since all of them are called with the term "green". However, the presence of this term does not ensure the sustainability of a process, so the environmental burdens derived from its performance must be considered.

Therefore, this study aims to environmentally analyse the different rutin extraction sequences performed on a large scale taking into account the life cycle assessment (LCA) methodology. This methodology considers the complete life cycle of the extraction sequence ("cradle-to-gate" approach) and allows identifying the main processes or key stages responsible for the environmental loads. Novel techniques will be compared with the traditional one (ethanol-based Soxhlet extraction) because it is the most used method for the extraction of flavonoids due to its simplicity and ease of maintenance (Chávez-González et al., 2020). The side-streams originated in the different recovery routes will be managed by anaerobic digestion, obtaining biogas and digestate, so that the biogas produced in the auxiliary activity will be valorized for energy recovery while the digestate presents potential as biofertilizer (Timonen et al., 2019).

2. Materials and methods

LCA methodology systematically evaluates the environmental aspects of a process, product or activity by analysing its associated environmental impacts during its life cycle stages (ISO 14040, 2006). This methodology has been followed in detail as well as its four phases: definition of objectives and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation of results (ISO 14040, 2006; ISO 14044, 2006). An attributional LCA approach is considered due to the use of average data in all the scenarios analysed (Ekvall, 2020).

2.1. *Definition of the scope and system boundaries*

The objective of this study is to evaluate the environmental performance of three scenarios that represent different valorization routes to obtain rutin as target product and digestate as by-product. When an LCA is performed, the functional unit must first be defined, since it provides the reference to which the inputs and outputs of the system studied are related (ISO 14040, 2006; ISO 14044, 2006). The functional unit in a biorefinery study can be selected based on the raw material or the quantity of the target product (Ahlgren et al., 2013), i.e. one kilogram of rutin.

The environmental impacts associated with the construction and installation of the biorefinery plant during its useful life have been considered negligible; therefore, no infrastructure process has been considered. This hypothesis is similar to assumptions made in other similar LCA studies (Jeswani et al., 2015; Karlsson et al., 2014). The storage stage is not included within the system boundaries, considering there is no chemical or energy requirement in the storage stage (Cortés et al., 2019).

As indicated above, rutin is obtained from the extraction of asparagus waste from the processing industry. This waste is the inedible part of the asparagus, considered as a waste in the food industry and which has a low (or even no) economic value on the market (Viera-Alcaide et al., 2020; Zhang et al., 2019). Therefore, the raw material of the proposed biorefinery plant is assumed to be a waste and therefore, the value of the environmental burdens arising from its production has been assumed to be zero (Liu et al., 2017; Thyberg and Tonjes, 2017). The system boundaries of this environmental study include the process units of each of the simulations studied, as depicted in Fig. 1. As mentioned above, three different valorization scenarios are studied, all of them composed by five subsystems (hereinafter SS); pre-treatment (SS1), extraction (SS2), solids removal (SS3), solvent recovery (SS4) and anaerobic digestion (SS5).

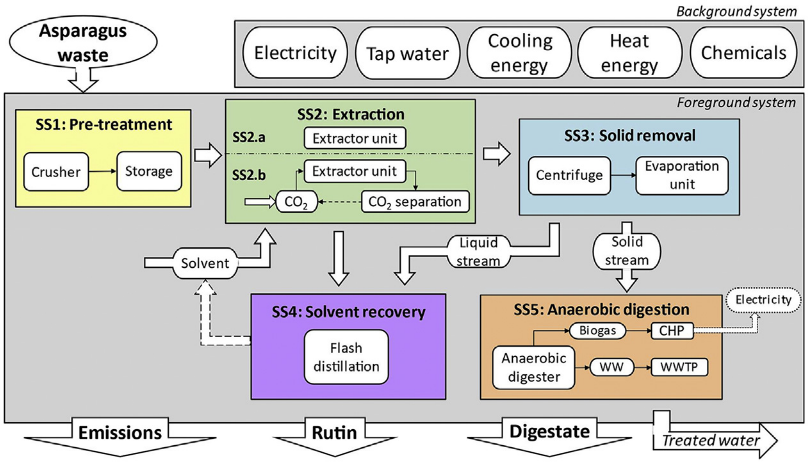


Fig. 1 – System boundaries of the scenarios proposed as a biorefinery strategy; SS2.a correspond to Scenario I (Soxhlet extraction) and Scenario II (Pressurized liquid extraction), SS2.b correspond to Scenario III (Supercritical fluid extraction). Acronyms: WW — wastewater, WWT — wastewater treatment, CHP — combined heat and power.

2.2. *General description of the scenarios*

Fig. 2 shows the different flow diagrams corresponding to the asparagus waste valorization to obtain rutin. As indicated above, three different valorization scenarios consisting of five subsystems are designed. SS1 and SS5 are identical in all the proposed scenarios (i.e., the same equipment and the same operating conditions).

SS3 and SS4 are designed with the same equipment but operate under different operating conditions. The main difference involves the selection of the extraction technique in SS2 for each scenario. The description of the subsystems is shown below.

- Pre-treatment stage (SS1): asparagus waste is crushed approximately 5 cm to promote the rutin extraction.
- Extraction stage (SS2): Soxhlet extraction, PLE and SFE are the methods used to obtain rutin in Scenarios I, II and III, respectively. The operating conditions of the different extraction techniques are:
  - ○ Soxhlet extraction: the operation is carried out at 100 °C at atmospheric pressure for 4 h (Solana et al., 2015) and ethanol is considered as base extractive agent for this extraction technique (Vangalapati et al., 2015). No specific data on rutin extraction yields from asparagus wastes using this procedure with different solvents have been found in the literature. Accordingly, the study developed by (Vangalapati et al., 2015) has been considered to estimate what would be the increase (or decrease) in the extraction yields. Thus, and bearing in mind the reported results, the use of ethanol instead of methanol as extractive agent should derive to a 17% decrease in the rutin extraction yield. On the other hand, using ethyl acetate, the decrease would be of around 67%.
  - ○ PLE: the extraction is carried out at 65 °C with a pressure of 10 MPa for 30 min. The solvent used is a mixture of ethanol and water (1:1) (Solana et al., 2015).
  - ○ SFE: it is performed at 65 °C and 15 MPa for 1 h. The extractive agent used in this technique is a mixture of ethanol and water (1:1) added to a CO_2 stream, in a ratio of 8% (w/w) with respect to the stream of CO_2. In addition, the flow of the gaseous stream is 0.25 ± 0.05 kg/h (Solana et al., 2015).

In this stage, two streams are obtained (see Fig. 1). The first one is made up of the solvent used together with the rutin and is derived to SS4 (solvent recovery). The second stream consists of the asparagus leftover with a small amount of solvent.

- Solid removal stage (SS3): the surplus stream from SS2 separates its solid fraction (asparagus leftover) from the liquid (solvent) in this subsystem by means of centrifugation and evaporation units allowing a greater amount of solvent to be recovered. The solvent stream recovered is sent to SS4. Evaporation takes place at 55 °C and 30.4 kPa in Scenarios I and III and at 67 °C and 30 kPa in Scenario II.
- Solvent recovery stage (SS4): flash distillation unit allows the recovery of the extractive agent from the output streams derived from SS2 and SS3. This distillation unit operates at 67 °C and 30.4 kPa in all the scenarios. The recovered solvent is recirculated (between 90 and 95%, depending on the scenario) to SS2 and, consequently, a closed-loop system can be achieved.
- Anaerobic digestion stage (SS5): the solid flow of SS3 (see Fig. 1) is digested under mesophilic conditions (≈35 °C) (Chen et al., 2014). The biogas obtained is transformed into electricity and used to reduce the energy required by the electrical equipment of the plant.

Finally, the digestate obtained, considered as a by-product of the biorefinery, can be sold as a biofertilizer for agriculture involving an economic benefit (Arias et al., 2020a).

2.3. *Life cycle inventory*

The life cycle inventory step consists of the collection of the quantitative input and output data for the system under consideration for the environmental assessment. This is done using primary or secondary data from publications or databases. In this study, the inventory data, such as the electrical needs of all equipment, consumption of chemicals, process water and thermal energy, have been obtained from simulations made with Aspen Plus® software, from the laboratory scale work developed by Vangalapati et al. (2015), Solana et al. (2015) and Santos et al. (2014).

The mass and energy balances resulting from process simulation are used as the basis for the LCI of each scenario (Table 1). The treatment capacity for the scenarios is 300

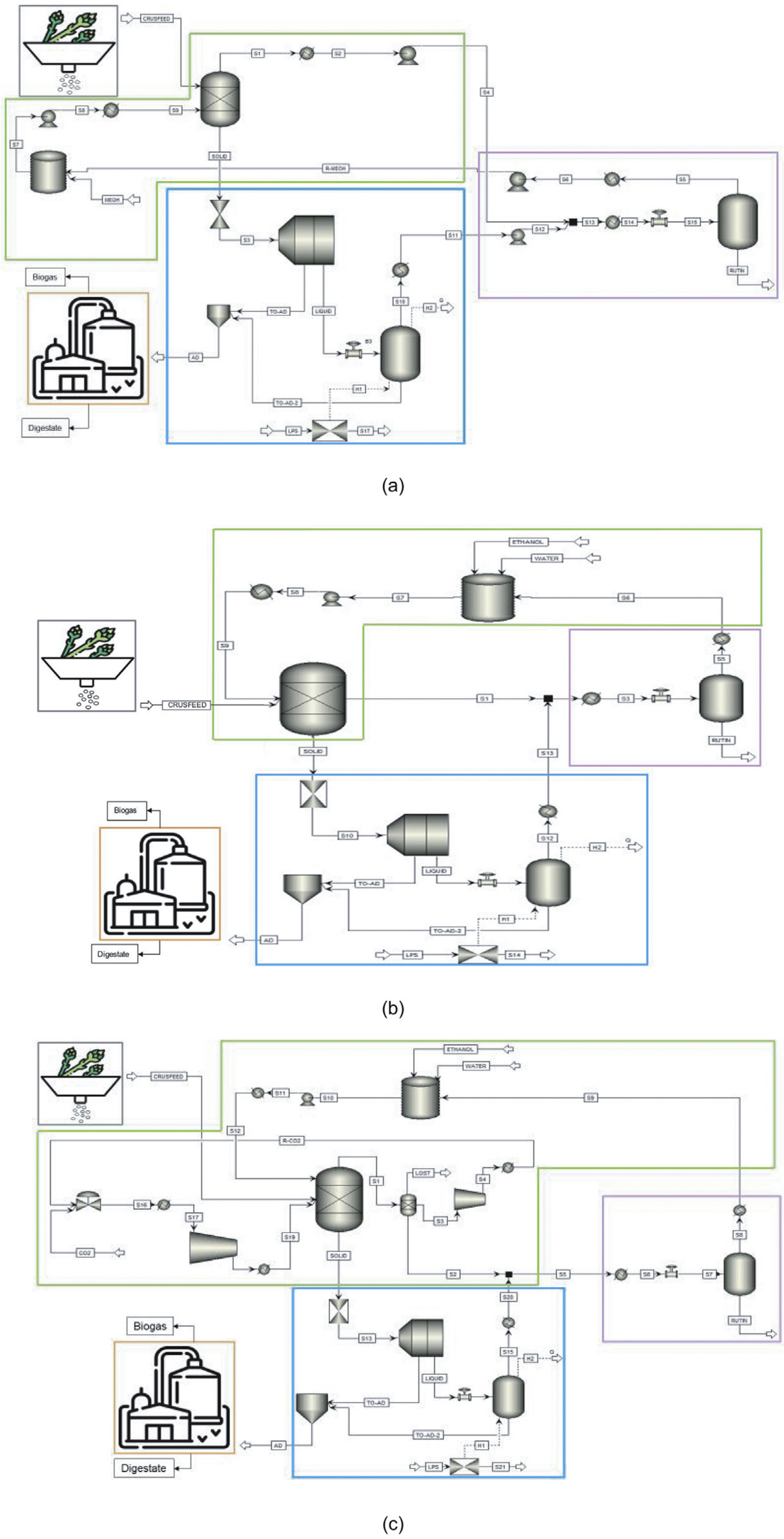


Fig. 2 – Aspen Plus flowsheet for (a) Scenario I (Soxhlet extraction), (b) Scenario II (Pressurized liquid extraction), (c) Scenario III (Supercritical fluid extraction). Grey box — Subsystem 1, green box — Subsystem 2, blue box — Subsystem 3, purple box — Subsystem 4, orange box – Subsystem 5 (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

kg of asparagus waste with a moisture content of 90%. The CO_2 stream is supplied from a bioethanol refinery, which is assumed to be in the surrounding area (González-García et al., 2018). This stream is an emission into air originated during the glucose fermentation stage to obtain ethanol. Bearing in mind the approach established for the asparagus stream entering in the plant, where no environmental loads were allocated assuming it as a waste (see Section 2.1), the same assumption has been considered for the CO_2 flow consumed in the plant.

In the environmental analysis, the heat source is obtained from the steam of the chemical industry, while the cooling energy consists of the recovery of the refrigeration util-

Table 1 – Life cycle inventory for the valorization of asparagus waste from all the proposed scenarios. Functional unit: 1 kg of rutin. Scenario I: ethanol-based Soxhlet extraction; Scenario II: PLE extraction based; Scenario III, SFE extraction based; Scenario I.a: methanol-based Soxhlet extraction; Scenario I.b: ethyl acetate-based Soxhlet extraction.

Inputs from technosphere	Scenario I	Scenario II	Scenario III	Scenario I.a	Scenario I.b
SS1: Pre-treatment stage					
Crusher (kWh_e)	26.0	26.0	26.0	26.0	26.0
SS2: Extraction stage					
Tap water (kg)	9.6	15.8	18.4	9.6	9.6
Ethanol (kg)	303.0	22.5	31.3	–	–
Methanol (kg)	–	–	–	304.2	–
Ethyl-acetate (kg)	–	–	–	–	346.5
CO_2 (kg)	–	–	300.0	–	–
Pump (kWh_e)	0.08	2.9	6.0	0.08	0.07
Extraction unit (kWh_{th})	58.5	3.7	456.4	58.5	58.5
Compressor (kWh_e)	–	–	299.0	–	–
Cooler unit (kWh_{th})	715.7	–	663.8	860.8	416.4
Heater unit (kWh_{th})	1192.7	25.5	63.0	1442.2	693.8
CO_2 separator (kWh_{th})	–	–	99.5	–	–
SS3: Solid removal stage					
Cooler unit (kWh_{th})	133.9	23.3	17.7	159.9	84.0
Centrifugation unit (kWh_{th})	14.9	14.9	14.9	14.9	14.9
Evaporation unit (kWh_{th})	90.4	139.8	87.7	110.8	50.1
Condenser (kWh_{th})	89.3	136.7	85.2	109.9	49.3
Reboiler (kWh_{th})	35.4	35.4	22.9	35.2	40.4
Natural gas (kg)	3.2	3.2	2.0	3.2	3.6
SS4: Solvent recovery stage					
Pump (kWh_e)	0.05	–	–	0.05	0.05
Condenser (kWh_{th})	261.3	651.5	427.2	314.1	146.4
Heater unit (kWh_{th})	34.6	12.8	36.4	24.1	25.2
Flash unit (kWh_{th})	226.7	596.9	385.8	288.9	121.2
SS5: Anaerobic digestion stage					
Tap water (kg)	4.8	4.8	4.8	4.8	4.8
Electricity (Wh_e)	64.0	64.0	64.0	64.0	64.0
Heat (kWh_{th})	2.0	2.0	2.0	2.0	2.0
Outputs to technosphere	**Scenario I**	**Scenario II**	**Scenario III**	**Scenario I.a**	**Scenario I.b**
Co-products					
Rutin (g)	70.3	65.4	68.6	84.1	28.1
Digestate (kg)	24.6	24.6	24.6	24.6	24.6
Waste to treatment					
Wastewater (from SS5) (dm^3)	5.0	5.0	5.0	5.0	5.0
Emissions into air					
CO_2 (kg)	6.3	6.3	6.3	6.3	6.3
CH_4 (g)	6.8	6.8	6.8	6.8	6.8
N_2O (g)	2.7	2.7	2.7	2.7	2.7
H_2S (g)	30.4	30.4	30.4	30.4	30.4

CO_2 — carbon dioxide; CH_4 — methane; N_2O — nitrous oxide; H_2S — hydrogen sulphide; kWh_e — electric kilowatt; kWh_{th} — thermal kilowatt.

ity in a cogeneration unit. This information is available in the Ecoinvent® database (Moreno Ruiz et al., 2018). Furthermore, the electricity mix used in the environmental analysis considers the current data on average electricity generation and import/export data in Spain for 2019 (Spanish Electrical Network, 2020).

The biogas obtained in the anaerobic digestion stage (SS5) is transformed into electricity in a cogeneration unit to be used as renewable energy in the plant, achieving a reduction in energy demand (Arias et al., 2020b; McAllister et al., 2011). To calculate the production of electricity from biogas:

$$Electricity\ \ production = Biogas \cdot M \cdot \rho \cdot LHV \cdot c \cdot N \qquad (1)$$

where;

Biogas: amount of biogas (per m^3).

M: methane content in biogas (in this case, 0.6 m^3 CH_4 m^{-3} biogas).

ρ: methane density (0.656 kg m^{-3} CH_4).

LHV: lower heating calorific value of methane (5 × 10^4 kJ kg^{-1} CH_4).

c: transformation coefficient (2.78 × 10^{-4} kWh kJ^{-1}).

N: efficiency of the cogeneration unit (in this case, 32%).

The same composition has been assumed for biogas in all scenarios, consisting of 60% CH_4, 39% CO_2 and 1% H_2S (Arias et al., 2020b). The amount of electricity produced per scenario is 873.1 Wh. This energy is considered as an output of SS5, but not from the system as it is recirculated to the biorefinery. Finally, Table S1 summarizes the detailed information of the data sources for the background processes.

2.3.1. *Allocation approach*

In multi-product systems, it is essential to allocate or share the impacts of the processes involved in the system between the products and co-products obtained when an attributional LCA approach is considered (Ahlgren et al., 2013). The allocation procedure can be based on mass, economic or energy aspects

Table 2 – Summary of the rutin and digestate obtain. Computation of the mass and economic allocation factors estimated for rutin production (SS1, SS2 and SS3). Market process references (Corden et al., 2019; Sigma-Aldrich, 2020).

	Rutin	Digestate (as biofertilizer)	Mass allocation	Economic allocation
Scenario I	70.2 g	24.6 kg	0.30%	99.9%
Scenario II	65.2 g	24.6 kg	0.30%	99.9%
Scenario III	68.5 g	24.6 kg	0.30%	99.9%
Market price	1.95 €/g	4.0 €/ton	–	–

(Ahlgren et al., 2013). By distributing the environmental burdens among the products, if some of them are produced in small quantities (see Table S1), it can become the target product of the production process from an economic perspective (Ahlgren et al., 2013).

Therefore, considering that the economic allocation may reflect the objective of the production process (in this case, the commercialization of the rutin), it is considered the most viable option. On the other hand, different conclusions can be drawn from the results obtained in determining environmental impacts (Ahlgren et al., 2013). Consequently, it is considered that a sensitivity analysis should be performed considering the mass-based allocation due to the large difference between the quantities of the products obtained (rutin and digestate). Furthermore, this allocation would not be affected by market price fluctuations, as it does not depend on those values.

Finally, since both the target product and the by-product have no energy purpose, it does not make sense to make an energy allocation to distribute the environmental burdens.

The mass and economic allocation factors have been calculated by the amount produced of each product and its potential market price obtained from the literature (Corden et al., 2019; Sigma-Aldrich, 2020). As noted above, all valorization scenarios consist of five subsystems (from SS1 to SS5), with SS1, SS2 and SS3 being the common ones to produce rutin and digestate, but SS4 is specific to rutin production and SS5 to digestate production.

Taking into account these considerations, Table 2 shows the quantities of rutin and digestate (by-product) obtained, as well as their prices in the market and the estimated mass and economic factors of rutin production.

2.4. *Life cycle impact assessment methodology*

For the environmental analysis the characterization factors reported by the Institute of Environmental Sciences of Leiden University are used (CML 2001 method v2.05) (Guinée et al., 2002). The choice of this method is due to the fact that the method contains the most common impact categories used in LCA (Acero et al., 2014). The computational implementation of the life cycle inventory data is carried out using the SimaPro v9.0.0 software (Consultants, 2019).

The following impact categories are evaluated: acidification (AC), eutrophication (ET), global warming (GW), ozone layer depletion (OD), human toxicity (HT), freshwater ecotoxicity (FE), photochemical oxidation (PO). Moreover, cumulative energy demand (CED) is evaluated too to identify the global energy requirements per scenario, employing the method developed by (Frischknecht et al., 2007). The rationale behind the consideration of these environmental impacts is based on literature reports (Gwee et al., 2020; Zhang et al., 2018b), studies in which biorefinery LCAs were carried out using agricultural waste to obtain high value-added products.

3. Results

3.1. *Global environmental results*

Fig. 3a shows the comparative profiles identified between the modelled scenarios according to each impact category selected for evaluation in terms of the functional unit (one kilogram of rutin) under an economic allocation perspective. First, to identify the scenario with the best environmental profile, i.e., the one with the lowest environmental burdens, the environmental burdens of the different scenarios must be quantified.

It should be considered that 99.9% of the environmental burdens of the common subsystems (SS1, SS2 and SS3) are associated only with the rutin production. Afterwards, the environmental hotspots will be identified as they should be considered for further improvement.

According to the results, Scenario III (i.e., the SFE technique) presents the worst environmental results in all the impact categories, except in AC and PO where Scenario I depicts the greatest impact. The reason behind the high environmental loads is the large amount of electrical energy that Subsystem 2 (extraction stage) requires in comparison with the other scenarios. In this scenario, the carbon dioxide needs to reach a high pressure to convert it into a supercritical fluid. Thus, this unit comprises approximately 90% of the total electricity required in Scenario III (see Table 1). It should be noted that the total electricity required in this scenario is almost 90% higher than the one required in the other scenarios. On the other hand, it is worth noting that the amount of cooling energy required to lower the temperature of the CO_2 gas stream is approximately 56% of the total cooling energy required in the plant.

The large contribution of Scenario I to PO is associated with the large amount of solvent required in this scenario and therefore, the background activities involved in its production. Attention should be paid to the fact that this scenario involves ethanol consumption that is about 93% and 90% higher than Scenarios II and III, respectively. Regarding the burdens in AC from Scenario I, they are mainly associated with the thermal energy used in the heating unit in SS2 (extraction stage) to heat the solvent.

On the other hand, Scenario II (PLE technique) has the best environmental profile, reporting the lowest environmental loads in all the impact categories evaluated. Scenario II shows a decrease of approximately 84% between the highest impact categories of Scenarios I and III. The reason for this decrease in environmental burdens is the low energy required in the activities involved in extraction compared to the other scenarios (between 58% and 98% less) in addition to the decrease in the solvent demand required at the extraction stage (as noted above).

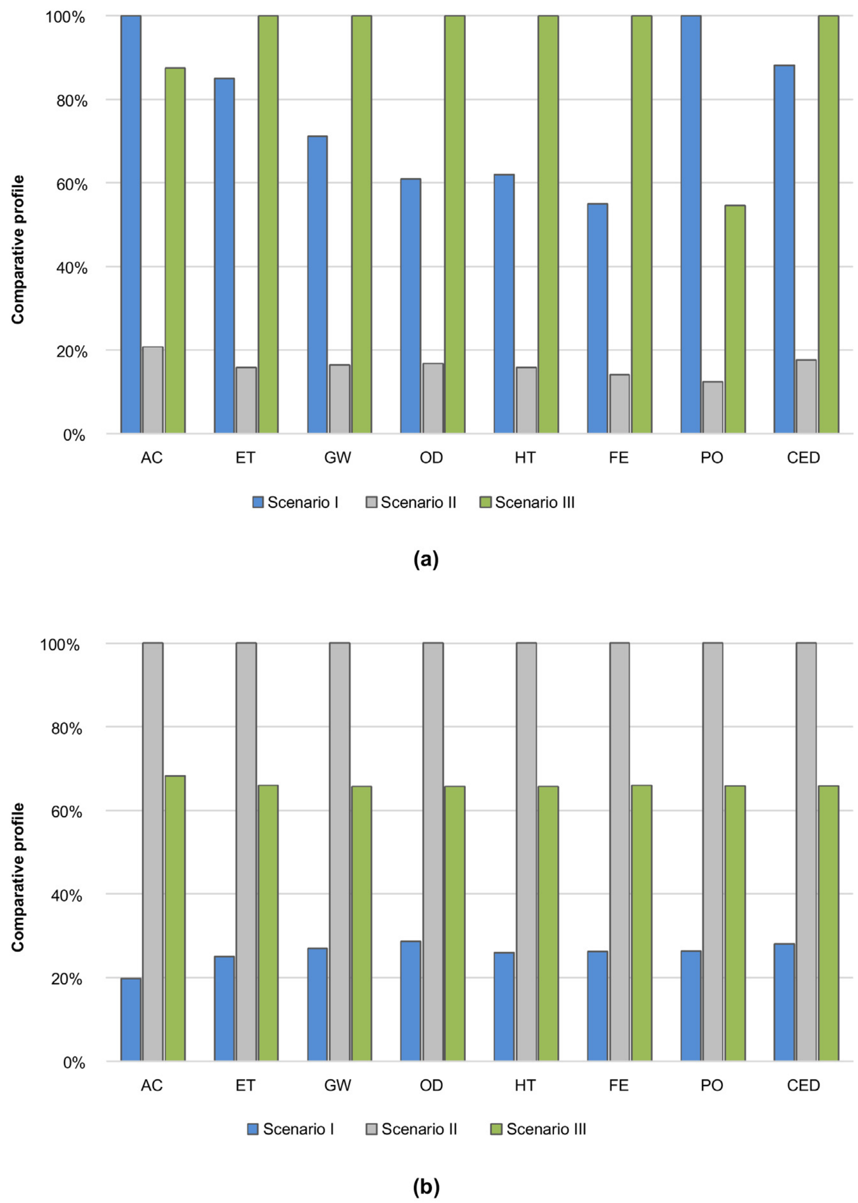


Fig. 3 – Comparative profiles for the different valorization scenarios under study (functional unit: 1 kg rutin); a) Economic-based allocation (base case); b) Mass-based allocation. Scenario I (Soxhlet extraction), Scenario II (Pressurized liquid extraction) and Scenario III (Supercritical fluid extraction). Acronyms: AC - acidification, ET - eutrophication, GW — global warming, OD — ozone layer depletion, HT — human toxicity, FE — freshwater ecotoxicity, PO — photochemical oxidation and CED — cumulative energy demand.

3.2. *Contributions of the proposed subsystems*

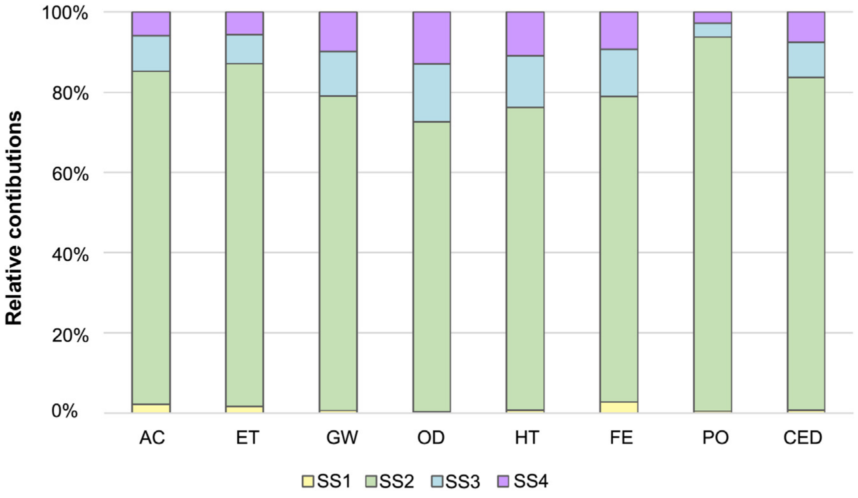
Fig. 4 depicts the distribution of environmental burdens by subsystems involved in the different extraction scenarios of rutin from asparagus waste, which allows the identification of the main hotspots of the different valorization scenarios. It should be noted again that an allocation of environmental burdens between SS1, SS2 and SS3 is carried out under an economic approach, with the allocation factor of 99.9% for the rutin production.

According to Fig. 4a, SS2 — the subsystem focused on the rutin extraction, is the one that plays a key role in the environmental profile associated with Scenario I (ethanol-based Soxhlet extraction), with contributions ranging from 72% to 93% depending on the impact category.

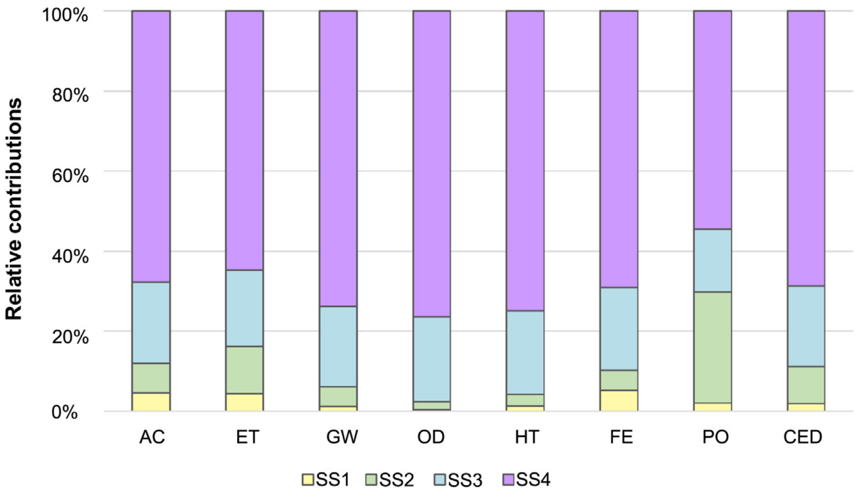
The reason of these outstanding contributions is due to the amount of thermal energy required to heat (1192.7 kW h) and cool (715.7 kW h) the extracting agent (ethanol). In addition, it is observed that in the PO category, SS2 represents approximately 95% of the total value, due to the background processes of ethanol production.

SS3 (solid removal) and SS4 (solvent recovery) contribute similarly to the profile with contributions ranging from 3% to 15% depending on the impact category. The rationale behind these figures is associated with the thermal energy requirements to perform the separation of the solid from the extracting agent (90.4 kW h in SS3) and to perform the flash distillation in SS4 (226.7 kW h). Finally, SS1 reports a negligible contribution to the global profile (below 3% in all categories). Electricity is the only requirement in this subsystem, being one of the lowest in comparison with the rest of the subsystems.

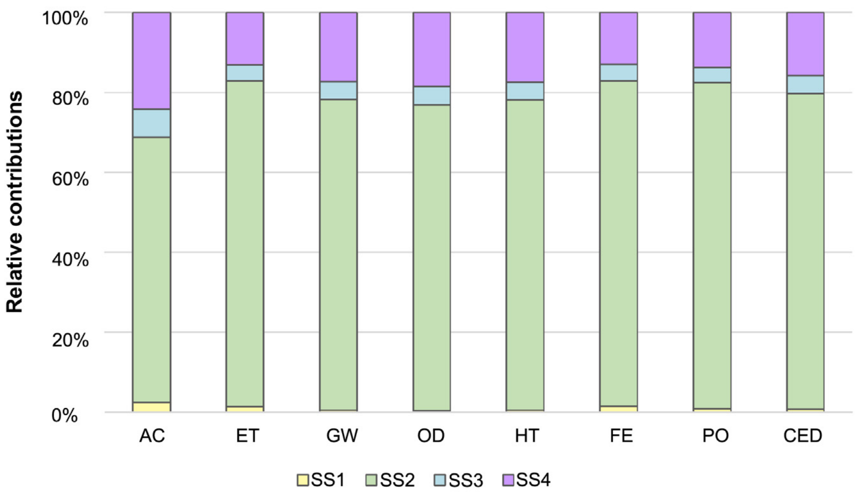
Fig. 4b shows the profile corresponding to Scenario II (PLE technique) where, unlike Scenario I, SS4 — the subsystem responsible for solvent recovering, is the one that performs an important function in terms of environmental burdens, reporting the highest contributions to all the impacts under



(a)



(b)



(c)

Fig. 4 – Distribution of environmental impacts per subsystems (SS) involved in the different valorization scenarios under economic allocation (functional unit: 1 kg rutin). (a) Scenario I (Soxhlet extraction), (b) Scenario II (Pressurized liquid extraction), (c) Scenario III (Supercritical fluid extraction). Acronyms: AC — acidification, ET — eutrophication, GW — global warming, OD — ozone layer depletion, HT — human toxicity, FE — freshwater ecotoxicity, PO — photochemical oxidation and CED — cumulative energy demand.

study, ranging from 54% to 76% regardless of the category. This subsystem consists of a flash distillation unit that is responsible for separating the target product (rutin) from ethanol, which will be recirculated to SS2 to close the cycle. To carry out this process, a large amount of thermal energy (651.5 kW h as detailed in Table 1) is required (approximately 73% of the global computation), being the main responsible for the high environmental burdens of SS4.

SS2 contributes significantly to the PO category (almost 28%). This is mainly due to the emissions derived from the production of ethanol required as an extractive agent (background process) and not recirculated in SS4. SS3 reports a consistent contribution in all categories (approximately 20%, regardless of the impact). This subsystem is responsible for solids removal after the extraction process takes place by separating the liquid fraction from the solid stream leaving SS2 through a centrifuge and evaporation unit, resulting in a solid waste stream, which is the input into SS5 (anaerobic digestion stage).

Finally, SS1 reports a negligible effect over the profile, below 5% for all impact categories. Electricity is the only energy consumption in this subsystem and no chemicals are required as in the other section. Therefore, this is the main reason for this low contribution, which still represents 56% of the total electrical energy needed in the scenario.

Finally, Fig. 4c shows the relative contributions reported by Scenario III (SFE technique). It can be seen that SS2 is the subsystem with the highest contributions to the environmental profile regardless of the category, ranging from 66% to 82%. The main reason of these figures is the outstanding amount of energy that this subsystem requires, both electrical and thermal, to carry out the rutin extraction.

The compressors are the equipment with the highest electricity consumption (≈86% of the total) compared to those required in the entire scenario (see Table 1). Compressors consume approximately 0.02 kW per kg of CO_2. This unit is used to compress the CO_2 stream to reach its supercritical state. As far as the thermal energy requirements are concerned, the extraction unit together with the refrigeration unit have the highest values in terms of thermal energy (around 40% and 56% of the total, respectively). The cooling unit is necessary to produce supercritical CO_2, while the extraction unit maintains the necessary temperature to carry out the extraction (i.e. 65 °C) by means of a heating jacket (Santos et al., 2014).

Continuing with the subsystems with higher environmental loads, SS4 shows a value between 13% and 24%, depending on the impact category. As in the other scenarios, this subsystem makes it possible to separate ethanol from rutin, managing to recirculate the solvent and obtain a product ready for sale. The evaporation unit is also responsible for the environmental loads of this subsystem due to the thermal energy it needs to perform its function.

Finally, SS1 and SS3 show very low-profile contributions. As can be seen from the results of the other scenarios, the values of SS1 are negligible because only electrical energy is required in the pre-treatment stage (SS1). As for SS3 (solids removal stage), only thermal energy enters this subsystem, it would be necessary to eliminate the from the output stream of SS2, which contains rutin and ethanol.

3.3. *Sensitivity analysis*

3.3.1. *Mass allocation*

As indicated above, mass allocation is used for this LCA study as an alternative to allocate common stage impacts between by-products, since different environmental outcomes could be obtained mainly due to different allocation factors. The mass allocation factors have been calculated considering the amount produced of each product (see Table 2). Accordingly, the amount of both rutin and digestate is divided by the total amount of both products obtained. Accordingly, it could be expected that not only the environmental profiles in terms of burdens change with the allocation chosen but also the preference ranking of scenarios.

Fig. 3b shows the comparative environmental profiles for the rutin-based valorization systems that are being considered for the mass allocation approaches. Based on the results, a large difference can be identified in the preference ranking compared to that of economic allocation (see Fig. 3a). Thus, the profile corresponding to Scenario II (PLE technique) is the one with the worst environmental profile, while Scenario I (Soxhlet extraction) is that with the best environmental profile, as

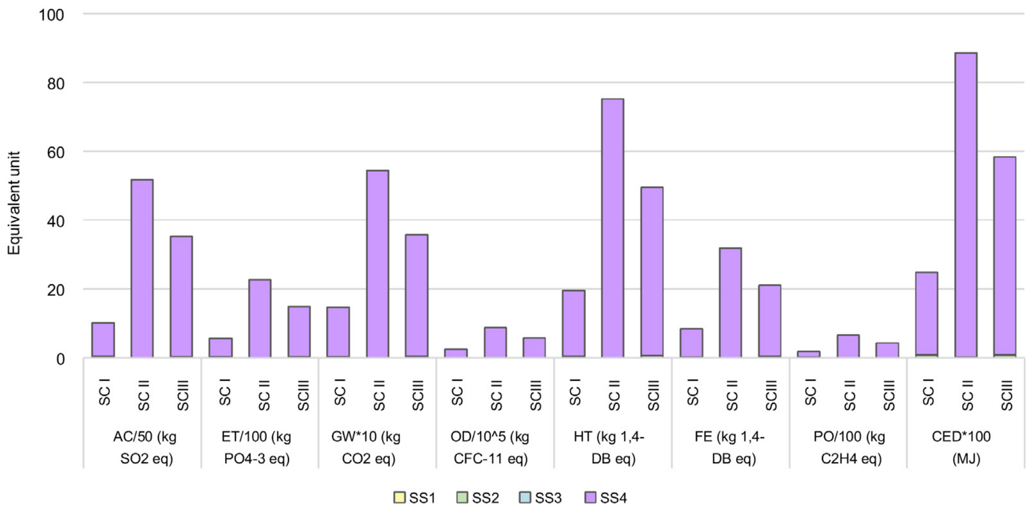


Fig. 5 – Distribution of environmental impacts per subsystems involved in the different valorization scenarios under mass allocation (functional unit: 1 kg rutin). (a) Scenario I (Soxhlet extraction), (b) Scenario II (Pressurized liquid extraction), (c) Scenario III (Supercritical fluid extraction). Acronyms: AC — acidification, ET — eutrophication, GW — global warming, OD — ozone layer depletion, HT — human toxicity, FE — freshwater ecotoxicity, PO — photochemical oxidation, CED — cumulative energy demand. SC I — Scenario I, SC II — Scenario II, SC III — Scenario III.

opposed to economic allocation where both present opposite outcomes.

In terms of characterisation results, environmental loads decrease on average by 34% in Scenario III (SFE technique) compared to Scenario II for all impact categories.

Regarding Scenario I, a surprisingly decrease of around 75% for all the categories studied is identified when mass-allocation is considered. The reason behind this behaviour is due to the low allocation factor for rutin production (0.30%), being therefore the environmental loads associated with SS1, SS2 and SS3 practically negligible within the global score. Thus, the entire weight of the environmental profile falls on the stage of solvent recovery (SS4), regardless of the scenario and the impact category.

This fact can be observed in Fig. 5, which shows the distribution of environmental impacts per subsystems involved in the different valorization scenarios under mass allocation. In all scenarios, energy consumption to recover the solvent in SS4 is the main responsible for environmental burdens being Scenario II the one with the highest energy requirement, mainly

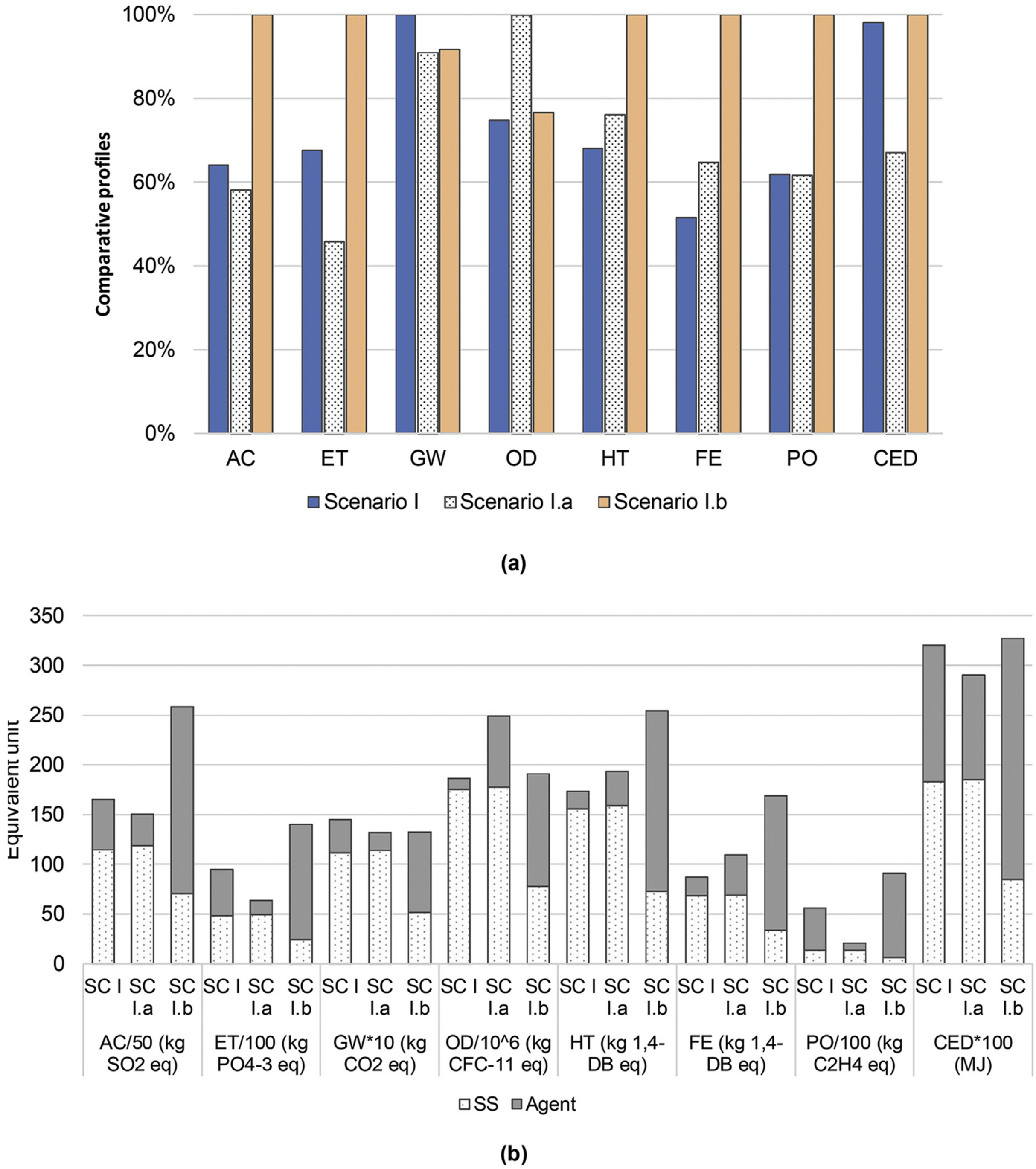


Fig. 6 – (a) Comparative profiles of the scenarios studied employed different extractive agents. (b) Distribution of environmental impacts per subsystems (SS) and extractive agent (Agent) production process involved in the Soxhlet extraction scenario employed different extractive agents. (functional unit: 1 kg rutin). Scenario I (ethanol-based Soxhlet extraction), Scenario I.a (methanol-based Soxhlet extraction) and Scenario I.b (ethyl acetate-based Soxhlet extraction). Acronyms: AC — acidification, ET — eutrophication, GW — global warming, OD — ozone layer depletion, HT — human toxicity, FE — freshwater ecotoxicity, PO — photochemical oxidation, CED — cumulative energy demand, SC I — Scenario I, SC I.a — Scenario I.a, SC I.b — Scenario I.b.

in the condenser cooling the vapor stream of the solvent at the outlet of the flash distillation (see Table 1).

Finally, a mention must be given to the by-product produced (digestate) in the biorefinery plant. If the data were reported per kilogram of digestate obtained, under a mass allocation approach, the results would show that Scenarios II and III would have the worst environmental profile.

The reason for this behaviour is that the common subsystems (SS1, SS2 and SS3) would have the highest environmental loads due to the great energy and chemical demand, reporting SS5, the specific subsystem of digestate production, negligible contributions due to the small amount of energy (without chemicals) required by the equipment involved in this subsystem.

Finally, when comparing the change from economic allocation to mass allocation (Fig. 5a and b), it can be observed how, depending on the impact category, the burdens decrease between 70 and 80% for Scenario I when using mass allocation. On the other hand, environmental burdens decrease approximately 35% in Scenario III in all impact categories when mass allocation is used instead of economic allocation. However, when comparing both assignments, it can be observed that in Scenario III the loads increase between 80–88%, depending on the impact category, when the mass assignment approach is used.

In summary, the selection of the allocation procedure considerably affects the results. In addition, attention must be paid to the economic allocation due to the instability of market prices, since they vary depending on supply and demand, as is the case of the rutin.

3.3.2. *Benchmarking the performance of organic solvents for rutin extraction*

The choice of organic solvents such as ethanol, methanol, and ethyl acetate will depend on the final use of the rutin. In the first study, ethanol is selected as the main extractive agent since it is a GRAS (Generally Recognized As Safe) solvent allowed by EFSA for food applications (EFSA, 2012). However, rutin has not only nutritional properties, but also cosmetic and pharmaceutical ones, allowing the use of other solvents for its extraction. Soxhlet technique is the standard method for solid–liquid extraction and still common in laboratories and industries (Chemat et al., 2020).

Two new valorization scenarios are designed taking as reference Scenario I described in Section 2.2. In addition, to know the amounts of methanol and ethyl acetate necessary to carry out the extraction as well as the yields, the study of (Vangalapati et al., 2015) is considered as reference. Table 1 shows the inventory data for these alternative scenarios, hereafter known as Scenario I.a and Scenario I.b when methanol and ethyl acetate are used as solvents, respectively.

Fig. 6a shows the comparative profiles of the alternative scenarios using different extractive agents. The analysis of the outcomes demonstrates that, in general terms, the environmental profile worsens with the use of the new solvents.

According to the results, Scenario I.b is the one that shows the worst environmental profile for all impact categories except for the OD and GW and OD categories. On the other hand, Scenario I.a presents the highest value for OD impact category, being 25% higher when comparing this category with the rest of the scenarios and, it can be observed that in Scenario I presents the highest value of the GW category, approximately 10% higher with respect to the other scenarios. The reason of the environmental load for the OD category is higher in the scenario based on the extraction with methanol is because a greater amount of energy is required to perform the extraction (SS2) as well as to recover the solvent (SS4). However, the reason why the GW is higher in Scenario I is due to the background activities involved in the production of ethanol (extractive agent in this scenario).

This point suggests the results shown in Fig. 6a since, although Scenario I.b (based on the extraction with ethyl acetate) is the one that presents the lowest energy requirements compared to the other two scenarios, the greater amount of solvent that is needs and the processes involved in its production are the main cause that this scenario is the one with the worst environmental profile. The results suggest that the ethyl acetate production is more polluting, compared to the other two solvents studied.

Fig. 6b shows the distribution of all the environmental impacts of the subsystems (SS1, SS2, SS3 and SS4) and the impact of the extractive agent production process of the scenarios based on Soxhlet extraction with different solvents. It should be noted that the contribution of SS2 is deducted from the environmental charges derived from the solvent production.

4. Discussion of the results. Comparative environmental analysis with different biorefinery studies

There are some references in the literature that have evaluated the potential of different extraction techniques on different target products. Therefore, a comparison with some of these references will be carried out to justify the results obtained in this environmental study.

As shown in Fig. 3 and Table S2, the "green" extraction technique based on supercritical fluids presents a better or worse environmental profile when compared to the other two extraction techniques, depending on the allocation approach. One of the main reasons for the high loads in almost all impact categories in SFE is the energy consumption required for the extraction step. The units for pumping/compressing and cooling the CO_2 stream are responsible for these energy loads, making them a conclusive factor for the high environmental loads derived from SFE process. The study of (Gwee et al., 2020), is based on the extraction of volatile oils from *Aquilaria sinensis* using supercritical carbon dioxide, under an environmental approach. An energy comparison shows that in this study and that of (Gwee et al., 2020), the energy required to cooling the CO_2 stream is approximately 40% of the total energy involved in the extraction stage. Similarly, the pumping/compression units are responsible, for both studies, approximately 20% of the energy consumption of the total stage. Therefore, looking at the same trend of energy consumption in both research works, as a possible future work, it would be convenient to evaluate and analyse different ways of cooling to reduce its environmental load as well as the reuse of the thermal output flows of the units that make up the biorefinery to reduce the energy consumption of the plant.

Among the different extraction techniques that have been considered in this study, it can be concluded that the extraction technique based on pressurized liquid can be considered as the most environmentally friendly technique, in accordance with the studies carried out by (Solana et al., 2015) and (Hirondart et al., 2020). Just to mention a few of its most outstanding advantages, the cost and speed associated with the process of extracting the flavonoid compound arise as the most relevant one. Moreover, a drastic reduction in the ecological footprint of PLE, up to 33 times lower than that of Soxhlet extraction.

When it comes to identify the main contributors in all impact categories, energy is undoubtedly the one that stands out clearly, although without jeopardizing the role of solvents. Although they can be recovered for reuse, it is inevitable that a smaller fraction must be added as fresh feed. If environmental impact indicators are analysed, such as the carbon footprint, this work reports a value of 2039 kg of CO_2 eq. per kg of rutin in Scenario III (see Table S2), comparatively lower than the value of 2364 kg CO_2 eq. per kilo of extract obtained with the SFE technique, reported by (Rodríguez-Meizoso et al., 2012).

The principle of the "green" extraction technique should be considered on the reduction of chemical agents and/or use of alternative agents (Chaves et al., 2020). In the work of (Kyriakopoulou et al., 2015) an environmental comparison was conducted between the Soxhlet, UAE and MAE techniques for the extraction of b-carotene from carrots. This study highlights the lower environmental impact of techniques that use fewer chemicals, such as the UAE and MAE, which are generally classified as g̈reen extraction techniques; compared to the conventional technique, with a decrease in environmental loads of near 68% in all the categories. According to the conclusions of (Kyriakopoulou et al., 2015), the MAE technique is the most environmentally friendly, compared to UAE and Soxhlet, due to its low extraction times. On the other hand, the Soxhlet technique is considered the worst technique due to the high amounts of time and solvent required to perform the extraction. Additionally, the results of the study by Ochoa et al. (2020) on the extraction of anthocyanins from purple yam using the UAE technique at laboratory scale, confirm again that the use of this novel technique performs better than conventional extraction techniques. For this reason, future research should focus on improving the scaling up of these novel techniques to industrial scale. A reduction of extraction times as well as solvent volumes would be an improvement for industries from both an environmental and economic point of view. Similar to this research work, (Aristizábal et al., 2019) carried out a comparative environmental analysis of different solvents such as ethanol, methanol and ethyl acetate. Our results reflect that ethyl acetate-based selection represents the worst option from the perspective of kg of CO_2 eq. per kg of solvent used, followed by ethanol and methanol, in line with the above-mentioned study. For this reason, the operating conditions of this conventional extraction process should be considered to decrease the solid/solvent ratio and reduce the burdens of the environmental profile. To conclude, it should be noted that energy is a key improvement point in all the proposed valorization scenarios. Process optimization (e.g., reuse of internal streams for heating/cooling other streams) as well as the use of renewable energy sources instead of the use of the national energy grid should be a future objective to improve the environmental profiles of these scenarios

5. Conclusions

The comparative environmental analysis based on the LCA methodology of different valorization scenarios of asparagus waste has been carried out to obtain rutin as the main high-added value product, under a biorefinery approach. Along with rutin, the digestate from an anaerobic digestion stage is also obtained as a co-product. The scenarios studied are based on the Soxhlet technique, pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE). Among the variety of techniques that can be used to extract rutin, it can be concluded the PLE method is the most environmentally friendly. On the contrary, despite being considered a "green extraction technique", according to this study, the SFE method is the one that contributes most to the environmental impact categories. However, when reporting the results under an economic allocation approach, the PLE-based scenario is the one that presents the best environmental profile. Conversely, when mass allocation is applied, it is this scenario that has the worst environmental profile for all impact categories. Despite the discrepancies found in the results obtained by one procedure or another, the LCA methodology makes it possible to establish a comparative framework that can represent a useful tool for identifying the advantages and disadvantages of each selected technique, as well as the possibility of identifying the operating parameters on which to act in the short and medium term.

Finally, taking into account that one of the techniques analysed is the most widely used and available in any laboratory: Soxhlet extraction, it is interesting to find out how to improve its environmental profile based on the most appropriate selection of solvents. The result of this environmental analysis shows as a first step that the change in solvent use modifies the environmental profile. The scenario using ethyl acetate has the worst environmental profile, while the scenarios using ethanol and methanol are quite similar from an environmental point of view.

Ethyl acetate production processes are the main cause of these higher environmental loads and its use in Soxhlet extraction is not considered a good option not only because of the low rutin extraction yield, but also because it is not environmentally friendly.

As future work, improvement of the operating conditions of the latest extraction techniques (PLE and SFE) should be considered because of their advantages compared to more conventional techniques (e.g., shorter extraction times and the use of a lower amount of solvents). Bearing in mind this optimization, it would be possible to achieve a better rutin extraction performance in addition to reducing the environmental loads derived from the use of solvents and the energy requirements, which are responsible for the highest environmental impacts of each of the profiles of the scenarios that use "green" extraction techniques.

Declaration of interests

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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.fbp.2021.08.005.

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