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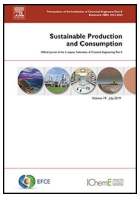

Life Cycle Assessment of various biorefinery approaches for the valorisation of almond shells☆

Leyre Sillero[a], Amaia Morales[a], Rut Fernández-Marín[a], Fabio Hernández-Ramos[a], Izaskun Dávila[a], Xabier Erdocia[b], Jalel Labidi[a,*]

[a] *Chemical and Environmental Engineering Department. University of the Basque Country UPV/EHU. Plaza Europa, 1, San Sebastian 20018, Spain*
[b] *Department of Applied Mathematics. University of the Basque Country UPV/EHU. Rafael Moreno 'Pichichi', 3, Bilbao 48013, Spain*

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ABSTRACT

In the near future, sustainable and efficient biorefineries would be essential for the production of commodity chemicals and high-added value compounds. Therefore, in this work, six scenarios differing on the delignification steps and cellulose conversion routes were assessed via Life Cycle Assessment methodology in order to study the environmental impacts derived from the conversion of an abundant agricultural residue (almond shells) into high added-value products and select the most suitable one for large-scale valorisation. The assessments were conducted employing experimental results and processing them by SimaPro software. The main conclusion achieved suggested that the enzymatic hydrolysis of the solid from any delignification step entailed the highest environmental impacts and had the highest relative contribution in all the studied impact categories with a maximum of 74%, which was ascribed to Scenario 5. It was also concluded that the organosolv delignification process affected overall more negatively than the alkaline treatment having bigger impacts especially in abiotic depletion (ADP) and photochemical oxidation (POP) categories. Finally, it can be stated that the best route for valorising the almond shell in a biorefinery facility is composed of autohydrolysis (common for every scenario), alkaline delignification, bleaching and acid hydrolysis steps for the obtaining of oligosaccharides, lignin and nanocrystals as products.

1. Introduction

Global concerns about fossil fuel depletion, climate change and the ever-growing global population have recently encouraged multiple technological, social and political innovations for the usage of natural resources rather than petrochemical ones (Mandegari et al., 2018). Many studies have shown that bio-based feedstock can be used for the production of good quality chemicals, materials and energy (Fridrihsone et al., 2020). Although the use of biomass has several advantages, the costly and sophisticated technologies employed for its transformation have meant serious limitations on its profitability and economic viability (Rahimi et al., 2018). In addition, occasionally inadequate environmental or socio-economic management may result in undesirable consequences. The increase in prices of basic foodstuffs and the proliferation of monocultures in the production of first-generation biofuels is a clear example (Nizami et al., 2017; Rahimi et al., 2018).

The transformation of the bio-based feedstock into biofuels or chemical products is commonly carried out in biorefineries, which can be considered the evolution of oil-based refineries that emerged in the 1940s. However, differing from the latter in which the concept of an integral valorisation strategy was obviated (Cardona-Alzate et al., 2020), biorefineries are designed to process or fractionate biomass integrally in order to maximise the outputs (Moncada et al., 2016). The biorefinery concept involves multiple processes such as pyrolysis, fermentation, gasification and incineration that have proven to be promising methods for converting non-food materials and residues (e.g. cereal straw, sugarcane bagasse, perennial grasses, corn stover, agricultural and forest wastes) into fuels and chemicals (Nizami et al., 2017). However, it is necessary to carry out an exhaustive analysis of the processes involved in a biorefinery to minimise, amongst other aspects, its environmental impact. This requires the reduction of water and energy consumption, as well as the elimination or replacement of environmentally

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* Corresponding author.
E-mail address: jalel.labidi@ehu.es (J. Labidi).

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Abbreviation

ADP	abiotic depletion potential
AP	acidification potential
CNC	cellulose nanocrystals
EP	eutrophication potential
FEP	freshwater aquatic ecotoxicity potential
GWP	global warming potential
HTP	human toxicity potential
LF	liquid phase
LSR	liquid to solid ratio
MEP	marine aquatic ecotoxicity potential
ODP	ozone depletion potential
POP	Photochemical oxidation potential
SL	solid phase
TEP	terrestrial ecotoxicity potential

harmful chemicals, such as chlorine, for others with less environmental impact. At the same time, it is imperative to increase performance and diversify the outputs. The outputs of a biorefinery highly depend on the input biomass, which is conditioned at the same time by its availability, abundance and geographical location.

Amongst the used biomass, the lignocellulosic one is gaining in popularity due to its availability, low competition with food crops and potential applicability as a sustainable source of many valuable products (Mandegari et al., 2018). Despite its composition varies depending on the feedstock species and origin, lignocellulosic biomass principally consists of carbohydrates (i.e. cellulose and hemicelluloses) and non-carbohydrate fractions such as lignin, proteins and extractives (Gullón et al., 2018; Yoo et al., 2020). Cellulose and hemicelluloses are present as polysaccharides in biomass and they can be converted into bioethanol, biobutanol and other fermentation products as well as into furan-based chemicals and other organic acids by both biological and thermochemical processes, respectively (Yoo et al., 2020). Nevertheless, proteins and lignin have also become promising candidates for the obtaining of other bioproducts, making the industrial implementation of lignocellulosic biomass-based biorefineries even more interesting (Dragone et al., 2020). Lignocellulosic biomass includes many agroalimentary wastes such as almond shells, which are produced in huge amounts worldwide and usually dismissed. However, many authors have shown their potential for the obtaining of added-value products from them (de Hoyos-Martínez et al., 2018; Fernández-Rodríguez et al., 2017; Morales et al., 2020). In the present study, the environmental impacts derived from the conversion of almond shells into high added-value products were assessed using the Life Cycle Assessment methodology. Six different scenarios were subjected to evaluation, which all had a first autohydrolysis step in common and differed on the delignification method, the bleaching step and the products obtained from cellulose (glucose or nanocrystals). The evaluation of the proposed processes allowed the identification of critical environmental hotspots. The study was developed according to laboratory scale experimental data, and the simulations, carried out with SimaPro LCA tool, leaded to the presented results.

2. Literature review

Almonds are one of the most produced and consumed nuts in the world (INC-International Nut and Dried Fruit, 2019). In fact, 2.1 million hectares of almond trees were cultivated worldwide in 2019, of which around 660,000 corresponded to Spain (FAOSTAT, 2020). Nevertheless, as for most nuts, the consumption of almonds implies the generation of large amounts of shells. It is estimated that between 70 and 150 million tons of almond shells are produced annually (de Hoyos-Martínez et al., 2018). Since no industrial or commercial application has still been found for this agricultural waste, they are usually burnt to recover energy or disposed into landfill without any control, causing many environmental problems (Kaur et al., 2020). However, this lignocellulosic residue could be further valorised via an integrated biorefinery approach in order to isolate added-value compounds, which would, at the same time, be beneficial for all the interested parts and would promote circular economy. Recently, almond shells have been selected as the feedstock for several biorefinery strategies (de Hoyos-Martínez et al., 2018; Fernández-Rodríguez et al., 2017), but to the best of our knowledge, there are no studies in which the environmental assessment of the complete valorisation of this or similar wastes have been performed.

Sustainability has become an important concept in the last years, especially due to the ecological and social challenges that the world has faced (Schramm et al., 2020). This term involves the study of environmental, economic and social aspects. These three aspects are evaluated by Life Cycle Assessment (LCA), Life Cycle Costing (LCC), and Social Life Cycle Assessment (SLCA), respectively, and their combination leads to a Life Cycle Sustainability Assessment (LCSA) (Schramm et al., 2020). LCA firstly appeared in literature in the 1960s, and it is nowadays defined as “a tool to assess the potential environmental impacts and resources used throughout a product’s life cycle, i.e. from raw material acquisition, via production and use stages, to waste management” ()(Dufossé et al., 2017). Thus, in order to determine the environmental impact of a biorefinery, it is necessary to conduct an LCA.

As shown in Table 1, several LCAs have been reported for different biorefineries. It was observed that each biorefinery implies the use of a feedstock (e.g. alfalfa, coffee cut stems, maritime pine, rocket plant, etc.) and that each feedstock can lead to a great variety of energetic as well as not-energetic (e.g. proteins, succinic acid, lactic acid, polyols, lignin, etc.) products, depending on the process to which it has been subjected. However, for these studies, multiple LCA tools have been used, which at the same time involve the election of the allocation methods and the impact categories to be studied. For this reason, comparisons between different LCAs are very difficult and they should be considered cautiously (Koch et al., 2020).

Amongst the displayed studies, there is no one related to almond shells. Kaur et al. explored different biological routes for the utilization of almond shells as bioenergy feedstock (Kaur et al., 2020). Nevertheless, they did not propose an LCA of their process. In this context, the present study aimed to assess and compare the environmental impacts of the conversion of almond shells into high added-value products through six different scenarios based on a previous experimental work (Morales et al., 2020) so as to identify the most environmentally friendly one.

3. Methods

Life Cycle Assessment (LCA) evaluates the environmental impacts of a product or service throughout all stages of its life. This process is standardised by international regulations ISO 14040:2006 (principles and framework for LCA) and ISO 14044:2006 (requirements and guidelines for LCA).

3.1. Goal and scope definition

The objective of this study was to evaluate the environmental impacts of several biorefinery routes for an integral valorisation of almond shell waste and its conversion into high added-value products. Each stage of the valorisation scenarios was performed at laboratory scale so as to have a more detailed overview of the

Table 1
Literature review of the existing biorefinery LCAs.

Input Biomass	Products	Scenarios	Impact categories	Reference
Alfalfa	Animal-grade protein Human-grade protein Press-pulp	6	5	(Corona et al., 2018)
Alfalfa stems Ethiopian mustard Poplar Flax shives Hemp hurds	Ethanol	1	5	(González-García et al., 2010)
Coffee cut stems Orange peel waste	Glucose hydrolysate Lignin Butanol	4	8	(Carmona-García et al., 2021)
Food waste	Combined heat and power Biofertilizers Single cell protein Biosuccinic acid Lactic acid	6	3	(Khoshnevisan et al., 2020)
Maritime pine	Wood (round, industrial, and residual)	1	11	(Ferreira et al., 2020)
Rapeseed oil	Polyol Condensate	1	9	(Fridrihsone et al., 2020)
Rocket plant	Biodiesel Bioethanol Biomethane Combined heat and Power Glycerol	3	3	(Rahimi et al., 2018)
Sugar bagasse and trash	Ethanol Methanol Lactic Acid	8	11	(Mandegari et al., 2018)
Sugarcane	Itaconic acid Polyhydroxybutyrate Succinic acid Combined heat and power	6	11	(Nieder-Heitmann et al., 2019)
Vine shoots	Antioxidant extract Purified hemicellulosic oligosaccharides Cellulose Lignin Glucose liquors Ethanol Energy	5	10	(Gullón et al., 2018)
Wheat straw	Lignin nanoparticles	1	6	(Koch et al., 2020)

proposed conversion schemes. Most of these experimental results were presented in a previous work (Morales et al., 2020). The suggested scenarios leaded to different products, such as a liquor rich in oligosaccharides, lignin, cellulose nanocrystals and glucose, which could be employed for further applications. A deeper description of the scenarios is given below.

Taking the goal and scope of this study into account, the selected functional unit (FU) was based on the amount of input biomass at the initial stage of the valorisation schemes, i.e. 1000 g of oven-dried almond shells. This FU is commonly used in LCA analyses that involve waste management systems (Gullón et al., 2018; Khoshnevisan et al., 2020) and it allows the comparison between the different schemes despite yielding different high added-value products. Moreover, due to the chosen FU, no allocation procedure was required and an attributional modelling approach was considered. The variety of the almonds shells employed was Marcona and they were provided by local farmers. The production batches were performed in a semi-pilot plant located in the Chemical and Environmental Engineering Department of the University of the Basque Country UPV/EHU (San Sebastian, Spain). The composition of the characterised biomass was: 16.7 wt.% cellulose, 31.6 wt.% hemicelluloses, 29.7 wt.% insoluble lignin, 3.1 wt.% ash and 3.7 wt.% extractives (Morales et al., 2020). The products obtained from the proposed six multi-output scenarios mainly derived from cellulose, hemicelluloses and lignin. The scenarios differed on the followed delignification processes and, hence, the type of lignin produced, as well as on the products obtained from cellulose (nanocrystals or glucose). The full system boundaries and process flow diagram for Scenario 4 is displayed in Fig. 1 and figures for the remaining scenarios (Scenarios 1–3; 5 and 6) in Supplementary data. As seen, the evaluated scenarios were considered to be cradle-to-gate systems but they did not involve the production of almond shells and neither their transportation to the semi-pilot plant nor the further conversion of the obtained products into materials, chemicals or other compounds.

3.2. Description of the biorefinery scenarios under study

In this work, 6 possible scenarios have been studied to obtain oligosaccharides, lignin, glucose and cellulose nanocrystals (CNC) from the point of view of an integrated biorefinery of almond shells.

All the scenarios have some subsystems in common, while others are different depending on the expected product. Firstly, the whole flow sheet of the process, with all the possible subsystems, will be described specifying in each specific step the differences that can be found depending on the scenario. All the scenarios started with the autohydrolysis of the almond shells, which were treated in a stainless steel Parr reactor with a liquid to solid ratio (LSR) of 8 (g/g in oven-dried basis), in isothermal regime at 179 °C for 23 min (SS1.1). These conditions were reported as optimal by Nabarlatz et al., and used by Morales et al. for the extraction

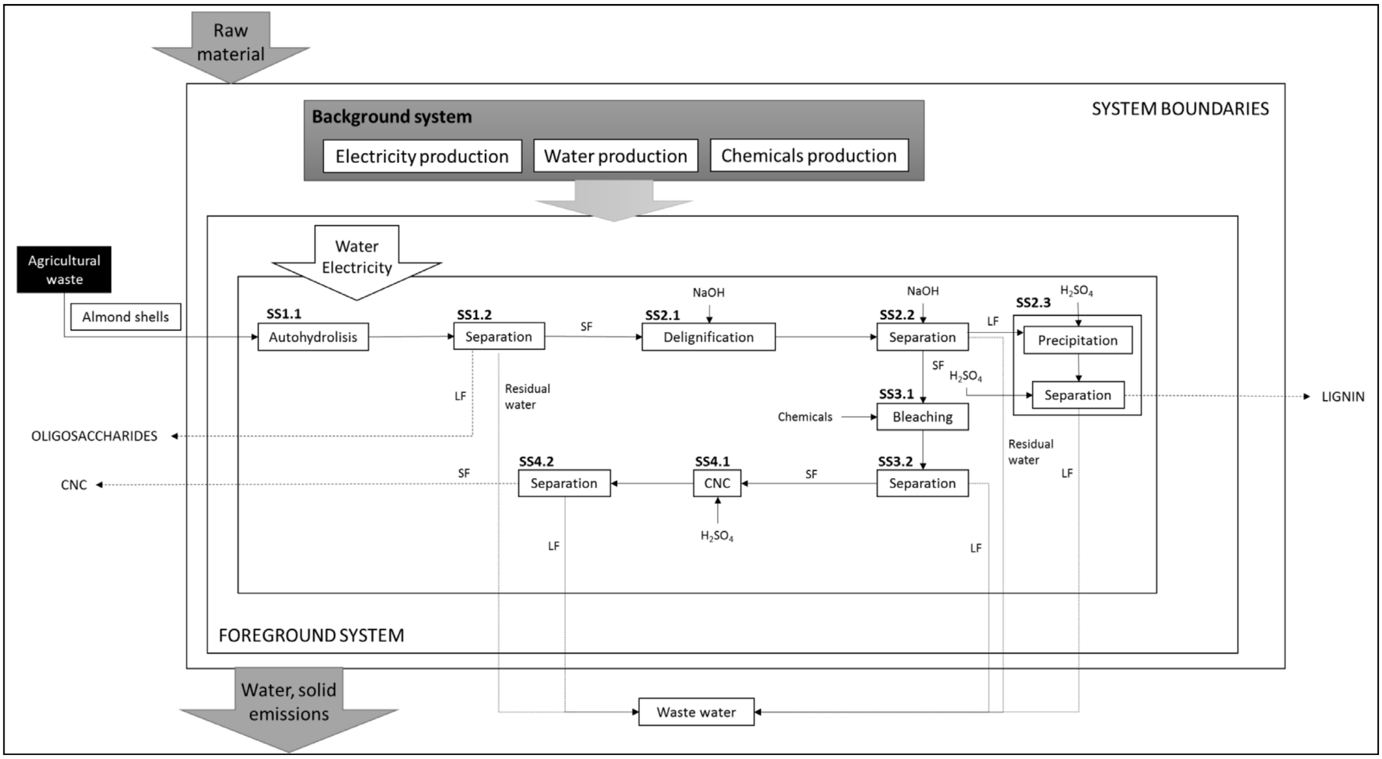

Fig. 1. System boundaries and process flowsheets for Scenario 4. All subsystems are supplied with tap water and electricity. Black boxes correspond to excluded processes. Acronyms: SF = solid phase; LF = liquid phase.

of oligosaccharides, making the solid more susceptible for the following stages (Morales et al., 2020; Nabarlatz et al., 2007). Despite this step being common for the six scenarios, it was included in each of them so as to obtain a cradle-to-gate environmental assessment. Once the autohydrolysis was completed, the system was cooled down until the system temperature reached 70 °C. After that, the mixture recovered was vacuum filtrated to separate the liquid and the solid fractions and the solid was washed with water (SS1.2). The obtained liquid phase (autohydrolysis liquor) was rich in a mixture of oligosaccharides, being the first extracted added-value product. The composition of the autohydrolysis liquor was reported by Morales et al. (2020).

Next step was delignification (SS2.1), which was carried out by two different methods depending on the scenario. For three of the scenarios (Scenarios 1, 2 and 3), delignification was carried out using organsolv treatment and in the other 3 (Scenarios 4, 5 and 6) using alkaline treatment. The organosolv and the alkaline processes were carried out following the conditions reported by Fernández-Rodríguez et al. (2017), and they were performed by Morales et al. (2020) to obtain the data used in this study. Briefly, the organosolv delignification treatment was carried out in a stainless steel Parr reactor using a LSR of 6 (mL/g) and 70% EtOH dissolution, at 200 °C and 90 min with constant stirring. Besides, the alkaline treatment was performed in an autoclave at 121 °C for 90 min using sodium hydroxide solution (7.5 wt.%) and a LSR of 6 (mL/g). In both delignification methods the obtained mixture was separated by vacuum filtration to obtain black liquors and the delignified solids, which were washed with water until neutral pH (SS2.2), obtaining cellulose rich solids. Lignin was obtained by precipitation from the black liquor (SS2.3). This step depended on the treatment used in the delignification, therefore, to obtain the organosolv lignin, the precipitation was carried out by adding two volumes of acidified water (de Hoyos-Martínez et al., 2018), while the precipitation of alkaline lignin was performed by acidification with H_2SO_4 until pH 2 (Dávila et al., 2017). Afterwards, lignin recovery was performed by vacuum filtration for all the scenarios and it was washed with water until neutral pH. After that, the next added-value products were obtained, i.e. organosolv and alkaline lignins, whose characterisations were reported by Morales et al. (2020).

In order to use the cellulose for the production of different products, such as glucose and CNC, a purification of the cellulose-rich solid was carried out by a bleaching treatment (SS3.1) in Scenarios 1, 2, 4 and 5. The solid obtained after the delignification process, was bleached with acetic acid and sodium hypochlorite in an oil bath at 75 °C during 2 h under constant stirring as it was previously described by Morales et al. (2020). After that time, the solid and liquid phases were separated by vacuum filtration, the solid fraction was washed with distilled water until neutral pH (SS3.2), and the liquid phase was discarded. Finally, in Scenarios 1 and 4, CNC were produced from this solid (SS4.1) by acid hydrolysis following the method previously described by Morales et al. (2020). Briefly, the solid was treated with 3 wt.% H_2SO_4 (ratio 1/15 g/mL) at 60 °C for 1 h in an ultrasound bath, and after that time, the reaction was stopped by adding distilled water. The suspension was vacuum filtered for the separation of the liquid fraction (waste) and the CNC, which were washed until neutral pH with water (SS4.2). CNC were the following added-value product obtained in this biorefiney scheme based on almond shells, and their characteristics were reported by Morales et al. (2020).

In Scenarios 2 and 5, after the bleaching process, the recovered solids were subjected to an enzymatic hydrolysis following the methodology described by Morales et al. (2020). In short, it was carried out at 48.5 °C in an orbital shaker with the Cellic Ctek 2 enzymatic cocktail, pH of 4.85, a LSR of 16 (g/g in oven-dried basis) and an enzyme to solid ratio of 20 FPU/g during 72 h (SS5.1). The obtained glucose rich liquid fraction was the last added-value product (Morales et al., 2020).

Table 2
Description of the subsystems that constitute each scenario.

Subsystem		Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
SS1	Autohydrolysis (SS1.1)	•	•	•	•	•	•
	Separation 1 (SS1.2)	•	•	•	•	•	•
SS2	Organosolv delignification (SS2.1)	•	•	•			
	Alkaline delignification (SS2.1)				•	•	•
	Separation 2 (SS2.2)	•	•	•	•	•	•
	Lignin precipitation & separation (SS2.3)	•	•	•	•	•	•
SS3	Bleaching (SS3.1)	•	•		•	•	
	Separation 3 (SS3.2)	•	•		•	•	
SS4	CNC production (SS4.1)	•			•		
	Separation 4 (SS4.2)	•			•		
SS5	Enzymatic hydrolysis (SS5.1)		•	•		•	•
	Separation 5 (SS5.2)			•			•

In Scenarios 3 and 6, as the bleaching treatment was not carried out, the mixture obtained after the enzymatic hydrolysis (SS5.1) was separated by vacuum filtration, obtaining apart from the glucose rich liquid fraction a lignin rich solid fraction, which was washed with water (SS5.2).

As mentioned before, the above described stages were all the subsystems considered for all the scenarios. However, each scenario had its own flow sheet containing only some of the subsystems as it is shown in Table 2.

3.3. Inventory data acquisition

Since data and their availability have a huge influence on the results of LCA (Schramm et al., 2020) it is important to collect high quality Life Cycle Inventory (LCI) data so as to be able to achieve a consistent and credible LCA (Gullón et al., 2018). The inventory data employed in the present work was composed of both, foreground and background data. On the one hand, foreground data involved the direct inputs to and outputs from each subsystem such as electricity requirements in all equipment (reactors, autoclave, shakers, etc.), chemical doses (H_2SO_4, NaOH, ethanol, etc.), tapwater and enzymes consumption, which were directly taken from the experimental results from the semi-pilot plant. As previously mentioned, all the stages of the valorisation schemes were performed in order to collect all mass and energy data (Morales et al., 2020). On the other hand, background data concerning the production and processing of the chemicals and energy carriers were retrieved from the Ecoinvent® (version 3.5) database. amongst the three types of models that this database offers, APOS (Allocation at Point of Substitution) model was selected.

The electricity requirements were estimated taking into account the power and the duration of the use of the equipments. Tables 3 and 4 show a summary of the input and output data involved in each scenario.

3.4. Environmental impact assessment methodology

LCA assesses and identifies environmental burdens, such as energy and resource consumption and environmental emissions associated with the life cycle of the process being evaluated (ISO 14040:2006). These burdens were analysed using the characterisation factors employed by the CML-IA baseline method developed by the Centre of Environmental Science of Leiden University, which is an update of the CML 2 baseline method. The latest is a European problem-orientated impact assessment method that involves obligatory impact categories that are used in most LCAs as well as additional and other impact categories. In fact, it gathers together the environmental burdens in midpoint categories such as abiotic depletion potential (ADP), acidification potential (AP), eutrophication potential (EP), freshwater aquatic ecotoxicity potential (FEP), global warming potential (GWP), human toxicity potential (HTP), marine aquatic ecotoxicity potential (MEP), ozone layer depletion potential (ODP), photochemical oxidation potential (POP) and terrestrial ecotoxicity potential (TEP). The software SimaPro 8 was used to perform the data inventory and the estimation of the characterisation stage.

3.5. Limitations and hypothesis for the calculations

In the Life Cycle Assessment of all scenarios, different hypotheses were made to limit the area of study. In this context, the delivery and milling of almond shells were excluded from the system. The filters used were not taken into account, neither was the solid phase obtained after the enzymatic hydrolysis of the bleached solid, since its weight was zero or negligible.

As for water, used in washing products and by-products, it was managed as hazardous waste. The water used in the cooling and heating of the equipment was not recycled.

The choice of materials was performed according to their geographical location. In the cases that it was possible, material was selected with the abbreviation ES or RER, representing that its origin is Spain or Europe, respectively. In case it was not possible, GLO (Global) was chosen. The information selected from the main processes in the Ecoinvent® database is provided as Supplementary data.

4. Results and discussion

4.1. Global environmental results

The environmental burdens of the six biorefinery scenarios proposed in this work were quantified by classifying the inventory data for the 10 categories considering CML-IA baseline method. The comparison of the environmental profile would permit the identification of the scenario with the lowest environmental burdens, which will be the most environmentally sustainable biorefinery approach. Studying in detail the environmental profile of each biorefinery approach, the steps responsible of the highest environmental burdens, the *hotspots*, could be identified and their modification could permit the reduction of the environmental problems associated with the scenario.

The proposed biorefinery scenarios have some steps in common which are the autohydrolysis treatment (SS1.1) followed by a filtration process (SS1.2), the delignification treatment (SS2.1) with the subsequent filtration process (SS2.2) and the precipitation of the lignin from the black liquor (SS2.3). Although the delignification treatment was present in all the scenarios, the process employed to remove the lignin from the autohydrolysis solids was different in half of the scenarios, in order to determine the most environmentally sustainable procedure. In the Scenarios 1, 2 and 3 an organosolv delignification process was employed while in Scenarios 4, 5

Table 3
Input data involved in each scenario.

Stage	Inputs	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Autohydrolysis (SS1.1)	Almond shells	1000 g (d.m.)	1000 g (d.m.)	1000 g (d.m.)	1000 g (d.m.)	1000 g (d.m.)	1000 g (d.m.)
	Tap water	186,928 g	186,928 g	186,928 g	186,928 g	186,928 g	186,928 g
	Electricity - reactor	25.2 MJ	25.2 MJ	25.2 MJ	25.2 MJ	25.2 MJ	25.2 MJ
Separation 1 (SS1.2)	Tap water	101,000 g	101,000 g	101,000 g	101,000 g	101,000 g	101,000 g
	Electricity - filtration	14 MJ	14 MJ	14 MJ	14 MJ	14 MJ	14 MJ
Delignification (SS2.1)	Tap water	183,575 g	183,575 g	183,575 g	3314 g	3314 g	3314 g
	Ethanol	1979 g	1979 g	1979 g	–	–	–
	NaOH	–	–	–	269 g	269 g	269 g
	Electricity - reactor	34.9 MJ	34.9 MJ	34.9 MJ	–	–	–
	Electricity - autoclave	–	–	–	34.2 MJ	34.2 MJ	34.2 MJ
Separation 2 (SS2.2)	Tap water	215,600 g	215,600 g	215,600 g	345,000 g	345,000 g	345,000 g
	Ethanol	1105 g	1105 g	1105 g	–	–	–
	NaOH	–	–	–	150 g	150 g	150 g
	Electricity - filtration	16 MJ	16 MJ	16 MJ	26 MJ	26 MJ	26 MJ
Lignin precipitation & separation (SS2.3)	Tap water	36,639 g	36,639 g	36,639 g	33,291 g	33,291 g	33,291 g
	H_2SO_4 (96%)	5 g	5 g	5 g	335 g	335 g	335 g
	Electricity - filtration	3 MJ	3 MJ	3 MJ	3 MJ	3 MJ	3 MJ
Bleaching (SS3.1)	Tap water	39,867 g	39,867 g	–	51,264 g	51,264 g	–
	Acetic acid	262 g	262 g	–	336 g	336 g	–
	$NaClO_2$	1568 g	1568 g	–	2016 g	2016 g	–
	Electricity - stirring	20.5 MJ	20.5 MJ	–	20.5 MJ	20.5 MJ	–
Separation 3 (SS3.2)	Tap water	7750 g	7750 g	–	9965 g	9965 g	–
	Electricity - filtration	4 MJ	4 MJ	–	5 MJ	5 MJ	–
CNC production (SS4.1)	Tap water	183,884 g	–	–	184,600 g	–	–
	H_2SO_4 (96%)	2034 g	–	–	2409 g	–	–
Separation 4 (SS4.2)	Tap water	946,845 g	–	–	1,121,400 g	–	–
	Electricity - filtration	71 MJ	–	–	84 MJ	–	–
Enzymatic hydrolysis (SS5.1)	Tap water	–	5286 g	6964 g	–	6251 g	8955 g
	Enzymes	–	52.5 g	69 g	–	62 g	89 g
	Citric acid	–	32.8 g	44 g	–	37.8 g	56.8 g
	NaOH	–	11.4 g	15.4 g		13.1 g	19.7 g
	HCl (37%)	–	15.2 g	21 g	–	18 g	26 g
	Timol	–	14 g	14 g	–	14 g	14 g
	Electricity - shaker	–	374.4 MJ	374.4 MJ	–	374.4 MJ	374.4 MJ
Separation 5 (SS5.2)	Tap water	–	–	69,312 g	–	–	89,268 g
	Electricity - filtration	–	–	6 MJ	–	–	7 MJ

Table 4
Output data involved in each scenario.

Stage	Outputs	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
Autohydrolysis (SS1.1 & SS1.2)	Oligossacharide-enriched liquor	8373 g	8373 g	8373 g	8373 g	8373 g	8373 g
Delignification (SS2.1, SS2.2 & SS2.3)	Lignin	78 g	78 g	78 g	107 g	107 g	107 g
CNC production (SS4.1 & SS4.2)	CNC	63 g	–	–	75 g	–	–
Enzymatic hydrolysis (SS5.1 & SS5.2)	Glucose liquor	–	243 g	248 g	–	334 g	317 g
	Lignin	–	–	106 g	–	–	181 g
Wastewater (SS1.2, SS2.2, SS2.3, SS3.2, SS4.2 & SS5.2)	Water for treatment	1,355,646 g	402,883 g	413,117 g	1,675,466 g	547,057 g	554,802 g

and 6 an alkaline delignification process was carried out. As it can be seen in Table 4, the alkaline treatment was slightly more efficient than the organosolv one, which influenced both the composition of the delignified solid and the products obtained during the revalorisation of the cellulosic fraction (Morales et al., 2020). To revalorise this last fraction, additional stages such as the production of CNC (SS4.1) and the enzymatic hydrolysis (SS5.1) have been considered, taking into account the desired final product. In the scenarios in which the CNC were produced (Scenarios 1 and 4) this step was preceded by a bleaching process (SS3.1). This last process was also carried out before the enzymatic hydrolysis in Scenarios 2 and 5, so as to have a solid rich in cellulose. However, Morales et al. (2020) appreciated that the bleaching process did not exert an improvement on the efficiency of the enzymatic hydrolysis.

Fig. 2 shows the environmental profile of the different biorefinery scenarios proposed in this work taking into consideration the different impact categories. According to the obtained data, the Scenarios 3 and 6 derived on the worst results in almost all the impact categories, except in ADP and ODP categories. In the case of ODP, however, the smaller impact was caused by the fact that the bleaching stage was not considered in this scenario, so it was free from the impact generated by the use of chlorine compounds. The difference between the Scenarios 3 and 6 were the conditions employed during the delignification treatment, and in most of the impact categories, the employment of one delignification condition or the other did not exert a significant influence on the environmental profile of the scenarios. However, for impact categories such as the photochemical oxidation (POP), the scenario in which the organosolv delignification (Scenario 3) was employed had a significantly higher effect than the Scenario 6, where the alkaline delignification was employed. In the case of abiotic depletion potential (ADP) and global warming potential (GWP) categories, the impact on Scenario 3 was slightly higher than in Scenario 6, while the opposite happened in the case of the ozone layer depletion (ODP). The small differences between carrying out an organosolv or an alkaline delignification treatment were also appreciated by comparing the environmental profile of the Scenarios 1 and 4 and the Scenarios 2 and 5. Nevertheless, the organosolv delignification had higher environmental issues than the alkaline procedure and this could be appreciated in impact categories such as abiotic depletion (ADP) and photochemical oxidation (POP). A similar be-

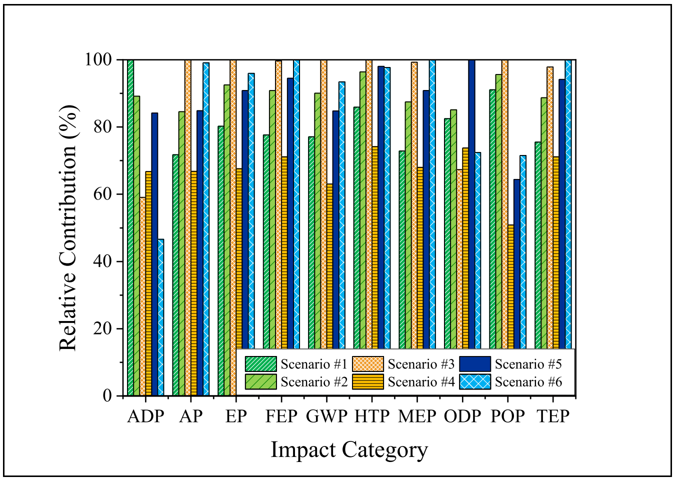

Fig. 2. Comparative profiles (%) for the different scenarios under study.

haviour was observed for organosolv and alkaline delignifications by Gullón et al. (2018).

To identify the cellulosic revalorisation procedure that exerted the lowest environmental impact the Scenarios 1 and 2 and the Scenarios 4 and 5 were compared, as in all of them the procedure to revalorise the cellulosic fraction was carried out after a bleaching treatment. It could be appreciated from the data shown in Fig. 2 that the environmental problems generated by the enzymatic hydrolysis were greatly higher than the ones provoked by the production of CNC, except for the ADP category, independently of the employed delignification conditions. Other authors also reported higher impacts for scenarios containing enzymatic hydrolysis, amongst other additional processes (Gullón et al., 2018).

Comparing the environmental profiles of the three scenarios in which the same delignification treatment was used (Scenarios 1, 2 and 3 or Scenarios 4, 5 and 6), shown in Fig. 2, it could be clearly appreciated that the biorefinery approach in which the production of CNC was carried out was the most promising one. However, in the case of the ADP and ODP categories, the least impact occurred in scenarios where the enzymatic hydrolysis without bleaching was conducted. Particularly, the Scenario 4 is the one with the lowest environmental burdens, as it had a lower effect on impact categories, such as ADP, GWP and POP than the Scenario 1, in which the CNC production was carried out after an organosolv delignification. Thus, the Scenario 4 was the most environmentally sustainable biorefinery approach that permitted the integral revalorisation of the almond shells by exploiting all the fractions of the feedstock.

4.2. Contributions per subsystems involved

Fig. 3a–c show the distributions of the environmental burdens involved in Scenarios 4–6 proposed for the valorisation of almond shells into high value-added products and the remaining distributions for Scenarios 1–3 are displayed in Supplementary data. These environmental burdens are separated by subsystems, so that the impact of each subsystem on the different scenarios can be analysed. The discussion of these scenarios was divided into two groups. On the one hand, the influence that the delignification conditions had on the environmental impact profiles of the scenarios was analysed by comparing Scenarios 1 vs. 4, 2 vs. 5 and 3 vs. 6, as they were formed by the same stages. On the other hand, the influence of the subsystems used for the revalorisation of the cellulosic fraction (SS3, SS4 and SS5) after the same delignification process was studied by comparing Scenarios 1 to 3 and Scenarios 4 to 6. It should be noted that the contributions of the autohydrolysis (SS1.1 and SS1.2) were equal for all the scenarios since the performed process was the same.

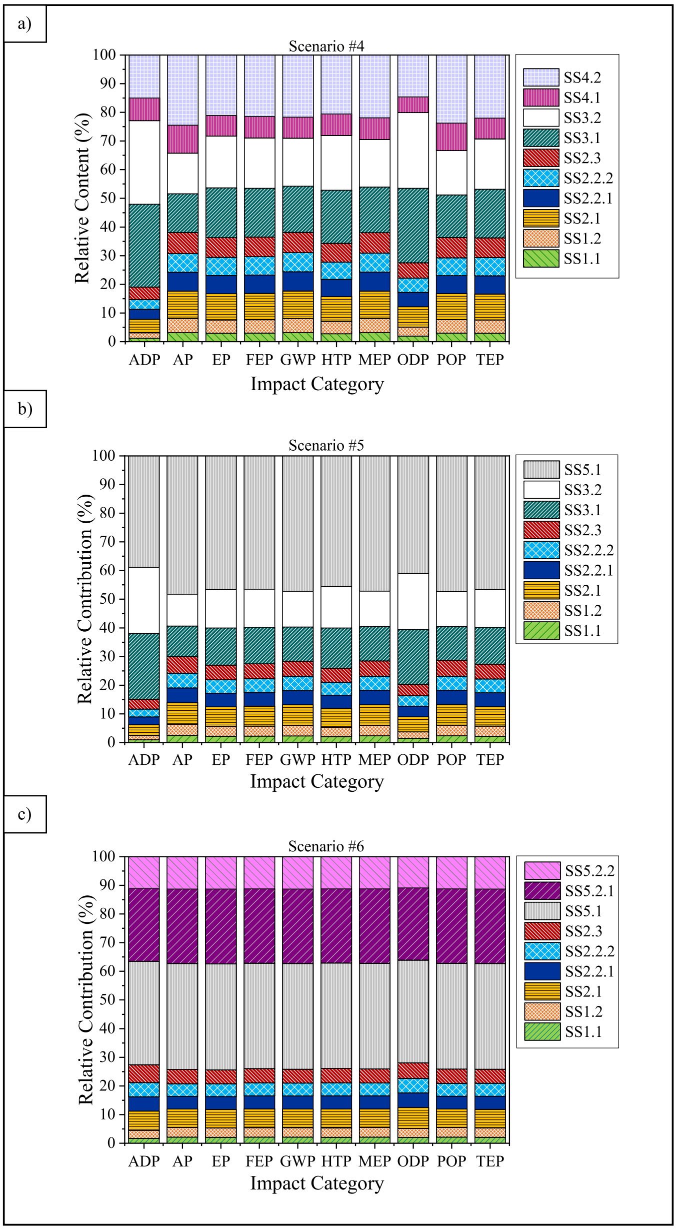

Fig. 3. Distribution of environmental impacts per subsystems involved in Scenario 4 (a), Scenario 5 (b) and Scenario 6 (c).

As it was appreciated during the analysis of the environmental profiles of the different scenarios in Section 3.1, the employment of the organosolv or alkaline delignification conditions did have a significant difference on the environmental impacts of the scenarios. This could be appreciated in the small differences that existed between the subsystems related to the delignification (SS2.1 and SS2.2) and to the lignin isolation (SS2.3) between the Scenarios 1 and 4, Scenarios 2 and 5 and Scenarios 3 and 6. These differences were slightly more significant in the ADP, POP and ODP impact categories.

The influence of the steps concerning the revalorisation of the cellulosic fraction (SS3.1, SS3.2, SS4.1, SS4.2, SS5.1 and SS5.2) accomplished between 57% and 80% of the environmental impact of the different biorefinery approaches. The lowest environmental burdens regarding the revalorisation of the cellulosic fraction were observed in the Scenarios 1 and 4, where the valorisation of the cellulosic fraction was carried out by CNC production (SS4.1 and SS4.2) after a bleaching stage (SS3.1 and SS3.2). It may be because of the high energy and chemical requirements of enzyme production (Feijoo et al., 2017) along with the electricity consumption during the enzymatic hydrolysis. Although the temperature at which this process was carried out was moderate (48.51 °C), the duration was very long (72 h), which made energy consumption rise (374.4 MJ). Analysing the scenarios in which enzymatic hydrolysis was used, it can be seen that in those scenarios where there was no previous bleaching treatment (Scenarios 3 and 6), this stage (SS5.1 and SS5.2) had a bigger contribution in all impact categories than in those scenarios where a previous bleaching stage (Scenarios 2 and 5) was used. This may be because in the Scenarios 2 and 5 a step was saved, since there was no need to separate lignin from glucose for its recovery. This was confirmed by comparing the average contributions of enzymatic hydrolysis (SS5.1 and SS5.2) in all the impact categories, which was around 45% for the Scenarios 2 and 5, and between 70 and 74% in the case of the Scenarios 3 and 6, respectively.

Regarding the scenarios in which nanocrystals were produced, Scenarios 1 and 4, some differences could be appreciated in the contribution of the bleaching treatment (SS3.1 and SS3.2) and the production of the CNC (SS4.1 and SS4.2) depending on the employed delignification method. When the organosolv delignification was carried out (Scenario 1), the production of the CNC was the hotspot, having the subsystem SS4.2 the highest environmental impact for all the categories, except for ADP, where subsystem SS4.1 had the highest value (21.57%). The contributions of subsystem SS4.1 range from 15.72% to 21.68%, closely followed by the contributions of subsystem SS4.2 ranging from 15.52% to 21.57%, depending on the impact category. However, when the alkaline delignification was carried out, the hotspot of this scenario was the bleaching process, as it could be appreciated in Fig. 3a. The subsystems SS3.1 and SS3.2 varied between 13.52–18.54% and 14.15–19.09%, respectively, for all the impact categories, except for the impact categories of ADP and ODP, in which their contributions are between 26 and 28%. This could be associated with the use of chlorinated compounds, which had a considerable impact on the abiotic environment.

Analysing the contributions of each subsystem to the different impact categories for the Scenarios from 1 to 6, it could be seen that, in the case of both autohydrolysis and delignification, subsystems SS1.2 and SS2.2 contributed in higher proportion to the impacts than the process itself (subsystems SS1.1 and SS2.1). This could be attributed to the high consumption of water required in the solids washing process, and consequently the high volume of waste generated. A comparison between the Scenarios 1 and 2 showed that, the contribution of the subsystems associated with autohydrolysis and delignification was slightly higher in Scenario 2 than in Scenario 1, with minimal differences. However, comparing the same scenarios but when alkaline delignification is used (Scenarios 4 and 5), greater differences were observed, and the trend was the opposite. In this case, the autohydrolysis and delignification subsystems had a greater contribution to the impacts in the Scenario 5. This happened because the process of nanocrystals production contributed more than the enzymatic process, so the overall percentages were increased in all subsystems. Finally, analysing Scenarios 2 and 3, which differ in the bleaching stage (subsystems SS3.1 and SS3.2), a large increase in the contribution of enzymatic process (SS5.1 and SS5.2) was observed in Scenario 3. This was due to the elimination of the bleaching stage, which provoked an increase in the general percentages of the contributions of all the subsystems, and especially in the aforementioned. Furthermore, the separation subsystem was added after the enzymatic hydrolysis, which increased resource consumption as well as the waste generation that should be properly disposed.

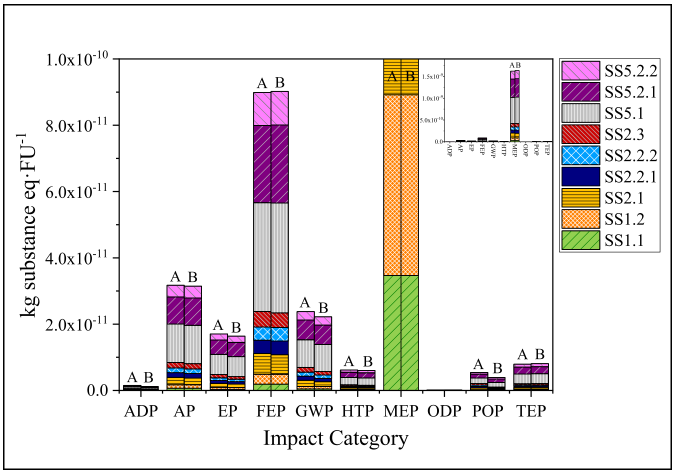

Fig. 4. Distribution of environmental impacts (characterisation results) per subsystems involved in Scenario 3 (A) and Scenario 6 (B), per functional unit.

Thus, during the analysis of the subsystems of the different scenarios it was appreciated that the enzymatic hydrolysis, the bleaching process and the nanocrystal production were the hotspots of the different biorefinery approaches.

4.3. Discussion of the results

After analysing the global and each subsystem's environmental burdens, it was concluded that Scenarios 3 and 6 were the ones presenting the worst environmental profiles. As displayed in Fig. 4, the delignification stage (SS2.1, SS2.2 and SS2.3) followed by the enzymatic hydrolysis (SS5.1 and SS5.2) reported the highest environmental impacts, especially in the cases of MEP and FEP categories. The contributions of the different responsible processes involved in each stage are depicted in Fig. 5. It should be mentioned that as the software considers the cumulative impact of the input solid in each stage, a big percentage of the overall impact was attributed to it. Therefore, in order to study the influence of the rest of the responsible processes (reagents and energy) their relative contributions were estimated without taking the input solid's effect into account.

As shown in Fig. 5a–d, electricity and tap water were common responsible utilities in all the analysed subsystems. It was clearly observed that the electricity had great impact in all the analysed stages but especially during the enzymatic hydrolysis (SS5.1 and SS5.2). During the first stage of the enzymatic hydrolysis (SS5.1), the electricity had a contribution of 80.5–98.3% in both scenarios. This high contribution is attributed to the heat and orbital shaking to which the samples were subjected for 72 h. The electricity in the second part of the enzymatic hydrolysis (SS5.2) was estimated from the energetic consumption of a vacuum pump. Nevertheless, this process was really carried out by vacuum filtering employing a compressor, which would probably consume less energy. The same happened for SS2.2 and SS2.3, where the black liquor and the delignified solid, and the lignin were separated by vacuum filtering, respectively. However, the electric impact was slightly lower on the first step of the delignification stage (SS2.1), especially in the case of organosolv delignification (Scenario 3) (22.3–88.8%). This might be ascribed to the high impact that other reagents such as ethanol had, which was more notable for ADP and POP categories, as reported by other authors (Gullón et al., 2018). On the contrary, tap water did not almost have a negative impact in the

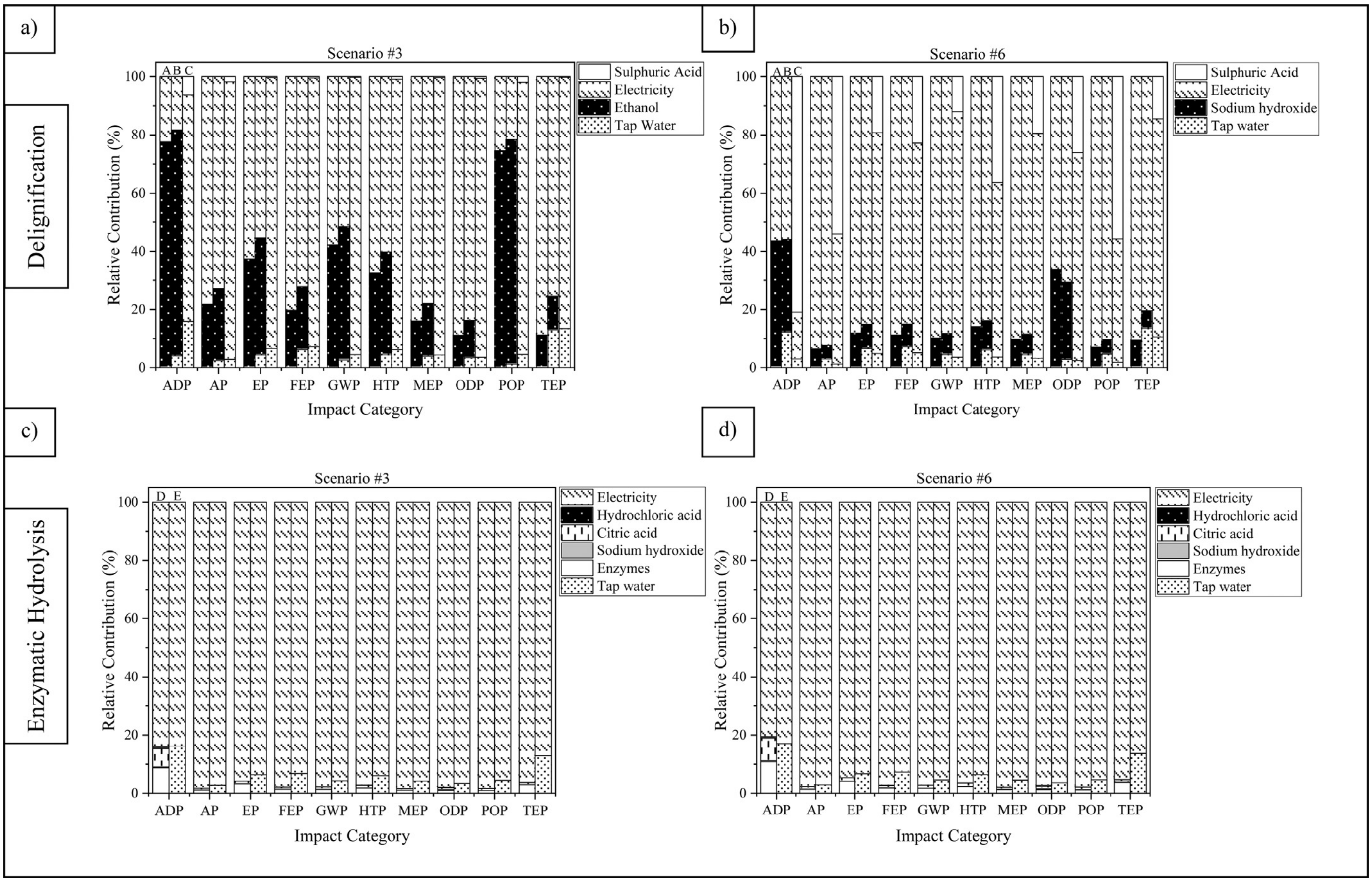

Fig. 5. Distribution of environmental impacts per responsible processes involved in the delignification (subsystems SS2.1 (A), SS2.2 (B) and SS2.3 (C)) and enzymatic hydrolysis (subsystems SS5.1 (D) and SS5.2 (E)) of Scenario 3 and Scenario 6, respectively.

studied subsystems, since despite using quite large quantities its influence was lower than 17% in any case.

As abovementioned, ethanol, which was responsible for organosolv delignification (SS2.1), had great impact in the case of Scenario 3, whereas sodium hydroxide had lower impact in Scenario 6 for alkaline delignification (SS2.1). However, sulphuric acid resulted to have an important impact in ADP, AP, HTP and POP categories in SS2.3 for Scenario 6, which was directly related to lignin precipitation. As the precipitation was done differently for alkaline and organosolv delignifications, the impact of sulphuric acid in Scenario 3 was considerably low.

Although its impact was almost insignificant, hydrochloric acid was expected to be a highly polluting reagent in SS5.1 due to its high content in chlorine, which is extremely hazardous to the abiotic environment and the ozone layer. Nevertheless, the main reason for its low influence could be that the employed volumes of this reagent were very little.

Citric acid also seemed to be slightly environmentally hazardous, in fact, its maximum contribution was found for ADP category and it was of 7.8%. Similarly, sodium hydroxide presented almost negligible effect in SS5.1 for both scenarios. Conversely, enzymes were found to be harmful to ADP category (8–10%) in both cases.

4.4. Sensitivity analysis

As abovementioned, the organosolv delignification had higher environmental impacts than the alkaline procedure, and as it can be observed in Fig. 5a for Scenario 3, ethanol is one of the main *hotspots* of the proposed biorefinery. Nevertheless, many authors have reported that this extraction can also be carried out with different organic solvents such as acetic acid, formic acid (Erdocia et al., 2014), methanol (Oliva et al., 2021) or glycerol (Martin et al., 2011). Therefore, a sensitivity analysis has been performed to this scenario in order to study the impact of using other solvents.

From Fig. 6, it can be concluded that, at first sight, methanol was the only solvent that seemed to improve the environmental impacts in all categories except for ODP. However, since methanol is highly toxic for living organisms, it entails higher risks in its employment in industrial processes and, thus, ethanol is the most used solvent for this kind of processes. In addition, ethanol permits the obtaining of highly pure lignin and a cellulose-rich solid to be processed downstream, while the products obtained from methanol delignification have not been deeply investigated.

In the case of the enzymatic hydrolysis, also performed in Scenario 3, although the required energy was detected as a *hotspot*, the alternative choices were not so facile. If the process did not imply the use of enzymes, it could be assisted by microwaves in order to reduce the energetic consumption, but as enzymes are involved, the only way to perform this reaction is as proposed in the present work. However, it is true that this reaction could be carried out chemically instead of doing it biologically and that microwave assisted method could then be used, but this would entail the enhancement of other impacts in spite of the reduction of the energetic demand.

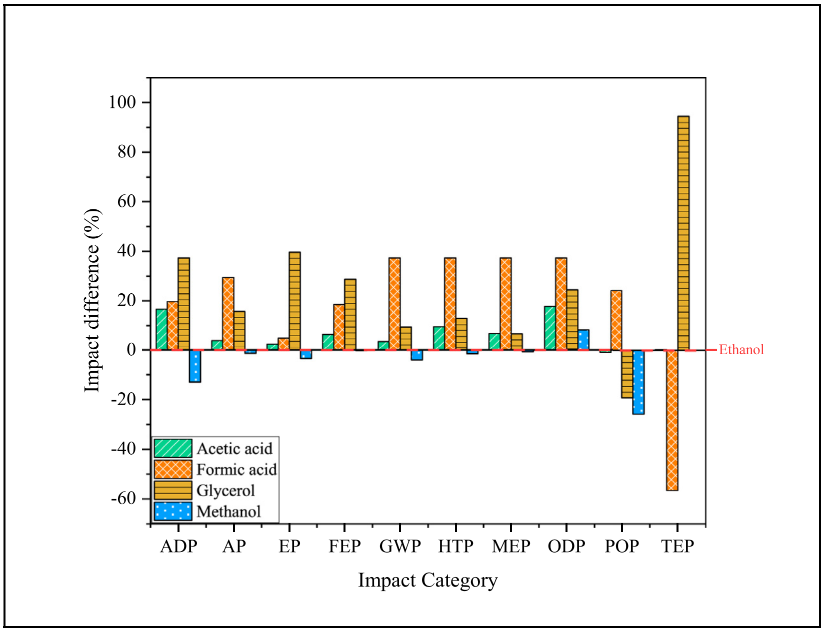

Fig. 6. Sensitivity analysis for Scenario 3 comparing the base scenario (with ethanol-organosolv delignification, taken as 0) with the impacts generated using other organic solvents. Positive differences imply the worsening of the environmental impacts, whereas negative differences mean improving them.

5. Conclusions and future directions

The environmental impacts of an integral valorisation of almond shells to obtain oligosaccharides, lignin, glucose or CNC through different biorefinery routes were assessed in this study. The LCA methodology employed allowed identifying the scenario with the lowest environmental burdens, which was Scenario 4. In this scenario, the target compounds were oligosaccharides, alkaline lignin and CNC. amongst the remaining scenarios, the Scenarios 3 and 6 presented the highest impacts in 8 of the 10 considered categories, suggesting that the obtaining of glucose and lignin without a previous bleaching treatment had very negative impacts regardless the delignification treatment employed. Moreover, by comparing these two scenarios, it was concluded that alkaline delignification had overall lower impact than organosolv delignification and, therefore, a sensitivity analysis was carried out so as to analyse alternative solvents. Methanol seemed to be the best option, but taking its harmfulness into account, ethanol resulted to be the most promising solvent.

This study allowed identifying the most environmentally friendly scenario for an integral valorisation of almond shells at industrial scale. Nevertheless, it should be noted that LCA studies are not enough for an in-depth sustainability assessment. Therefore, advanced sustainability assessment tools such as exergy, exergoeconomic and exergoenvironmental analyses should also be performed in the future.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.spc.2021.07.004.

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