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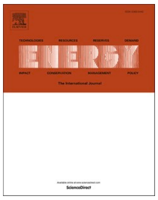

Benchmarking composting, anaerobic digestion and dark fermentation for apple vinasse management as a strategy for sustainable energy production

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ABSTRACT

Looking for renewable energy sources is one of the main targets in the transition to low-carbon economies. Bioenergy appears as an alternative with great potential, but firstly, it requires addressing all aspects that can limit its environmental viability. Stillage has been identified as an environmental concern of the bioethanol production. Thus, eco-friendly strategies for valorizing this resource should be pursued. In this work, three strategies such as composting (non-energy valorization), one-stage anaerobic digestion (with the aim of biogas production), and dark fermentation followed by anaerobic digestion (scheme under development to produce biohydrogen and biogas) were evaluated under a life-cycle perspective; and through process modeling based on literature data. The aim is to identify the advantages and disadvantages of dark fermentation for the management of apple stillage. To do this, a cradle-to-gate and attributional framework were followed, considering impact and damage perspectives. Results showed a very significant environmental load (around 99%) of composting compared to the selected energy recovery schemes, considering the added value of compost and the associated emissions versus those of biofuels. Otherwise, small differences were found between single-stage anaerobic digestion and dark fermentation (up to 16%), mainly, due to changes in chemical consumption and organic matter degradation efficiency.

1. Introduction

The strong dependence of energy and consumer goods on fossil resources requires the search for renewable sources to address the needs of society. It highlights the role of bioethanol as one of the most widespread biofuels, as well as the potential to use different types of renewable feedstocks, including waste streams from production processes [1]. The fermentation process also generates residues that require proper handling, such as vinasse, straw, bagasse, filter cake or molasses [2]. As an example, it is estimated that from 1 L of bioethanol, about 12 L of stillage is obtained [3]. This stream represents a valuable source of nutrients (N, P, K), which motivates its use in agricultural activities, mainly related to direct application for fertigation and soil erosion control [4]. However, its excessive application can modify soil pH and conductivity, and lead to eutrophication problems associated with nutrient leaching [5].

Several treatment strategies have been proposed in the literature to address the environmental concerns of stillage management. Some of them, such as aerobic treatment for the removal of nitrogen and organic matter, membrane technologies for wastewater concentration [6] and composting [7], are mostly applied, although it is desirable to promote other alternatives that add value to the process. In this case, the valorization of this stream with a view to produce biofertilizers, bioproducts, bioenergy and biomass is envisioned [8]. Considering the field of bioenergy as an urgent demand, it is a priority to define strategies in favor of energy products. One of the most popular bio-based energy valorizing alternatives is anaerobic digestion [9]. This waste management strategy fulfills the requirements of the zero-waste philosophy and simultaneously reduces the energy losses from the metabolic activity of the microorganisms. The carbon compounds are not being transformed to their fully oxidized state to other energy-containing chemicals. However, and in contrast to other valorization schemes such as aerobic composting, anaerobic digestion is not a self-heating process [10]. The energy from the bioproducts manufactured needs to be compensated by its energy demand. The result is a disagreement about the best

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Nomenclature

C	Composting scenario
COD	Chemical Oxygen Demand
D	Anaerobic digestion scenario
EC	Ecosystems
F	Dark Fermentation with Anaerobic Digestion scenario
FE	Freshwater Eutrophication
FRS	Fossil Resource Scarcity
FU	Functional Unit
GWP	Global Warming Potential
HH	Human Health
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LU	Land Use
ME	Marine Eutrophication
RR	Resources
SBR	Sequencing Batch Reactor
TA	Terrestrial Acidification
TN	Total Nitrogen
TP	Total Phosphorus
TS	Total solids
VS	Volatile solids
WC	Water Consumption

technology performance and a continuous race to optimize the process. While composting is more profitable at small scales and for the treatment of solid-state substrates composed mainly of cellulose and hemicellulose; anaerobic digestion has lower direct greenhouse emissions, leachate production, land occupation and increases the mineralization rates of nitrogen [11]. All seems to indicate that the selection of the valorization management strategy is strongly interlinked to specific purposes, rather to stand solely for one of them.

Meanwhile this debate has been produced inside the scientific community, the European population is nowadays struggling with a sharp increase rate of energy prices (11% for electricity between 2021 and 2022 compared to 2.5% in the period 2019–2020) and a decrease of availability [12]. Accordingly, the production of energetic "green" gases might help release the actual market pressure and move forward to a decarbonized production. Although the methane upgraded from biogas is the major bioenergy carrier in Europe (of the 32 TWh produced through biomethane around 90% came from anaerobic digestion) some of the other target products would be biohydrogen and biodiesel [13].

Bio-based H_2 production can be carried out in processes with sunlight or artificial light: biophotolysis and photofermentation, or light-independent: dark fermentation and microbial electrolysis. In the case of the dark fermentation process, there are advantages and disadvantages to consider for its implementation. It can treat a variety of substrates with a simple reactor design, but the H_2 production yield is low and requires additional treatment [14]. The incorporation of an anaerobic digestion (AD) process (also named as two-stage anaerobic digestion) through a serial sequence improves the overall process indicators through the production of hydrogen and biogas [15]. Moreover, the AD alternative is widely studied and its implementation on an industrial scale is feasible [16]. Compared to the single stage anaerobic digestion for the biogas production, the dark fermentation-methanation system increases the overall organic matter utilization of the stillage and provides a more stabilized digestate [17]. For example, Albini et al. [15] proved that the efficiency of the stabilization increased around 6.5–40.6%.

For this reason, this work addresses the performance, experience and innovation in the combination of dark fermentation and anaerobic digestion processes in order to close the biogas and biohydrogen cycle from an agri-food waste stream from a bioethanol production system. The environmental profile of a complex system must incorporate exhaustive information on all the processes involved in its life cycle, i.e., the holistic perspective of Life Cycle Analysis (LCA) will allow the identification of the environmental impacts for each and every stage of the process: from the management of raw materials, the production process as the core stage and the final use of biofuels, including the emissions associated with each of these stages. Recently, the literature review by Masilela and Pradham [18] identified the first dark fermentation LCA studies focusing on bio-based production, vehicle operations, thermophilic biological processes and feedstock influence. While this study is interesting as it addresses environmental analysis at laboratory and pilot scale, a more in-depth analysis is still pending in which the scope is broadened when considering the integrated process at industrial scale.

According to the aforementioned review, most of the waste used as feedstock for the production of H_2: rice husks, sugar cane juice, potato steam husks, wheat straw are of lignocellulosic nature. A potential raw material, due to its high level of production and consumption, could be the apple waste produced in the juice industry. The fraction of apple pomace represents 25–30% of the weight of fresh fruit, with a production volume of four million tons in 2020 [19]. An alternative for this stream could be the production of bioethanol, so that the stillage obtained as a by-product of this process has potential for recovery due to its high content of organic matter, potassium and calcium in its chemical composition, as well as moderate amounts of nitrogen and phosphorus [20].

The valorization of apple stillage for the joint production of H_2 and biogas may represent a viable strategy to reduce the large volume of this by-product on an industrial scale and serve as a new alternative to promote low-carbon energy generation. This study deals with an environmental analysis of the valorization of stillage from the fractional distillation of bioethanol produced from apple pomace. A double objective was followed to provide information on, firstly, the comparative assessment of three apple stillage management considering composting (as the mostly applied strategy, but with a non-energy valorization purpose), anaerobic digestion (as a reference energy process) and dark fermentation (as a potential technology under development). Thus, different levels of innovation are under evaluation in order to identify the one that obtains the best environmental performance. Secondly, and focusing on the strategy of interest, the identification of critical hotspots of the dark fermentation process by modeling different operating conditions at an early stage of design. In this regard, the LCA methodology is used to support the decision-making process for the environmental optimization of dark fermentation as a win-win solution. To the knowledge of these authors, this is the first study to carry out an environmental LCA approach to the valorization of fruit stillage. A cradle-to-gate attributional analysis has been carried out taking into account both midpoint and endpoint categories to provide a broad environmental perspective on both potential impacts and damages.

2. Materials and methods

2.1. Process description

The assessment of the environmental profile of processes under development through the Life Cycle Assessment methodology requires an initial stage of conceptual design of the full-scale process using modelling tools for different potential scenarios. In this case, three alternatives for the valorization of apple stillage were considered, according to the composition and characteristics reported by Hernández et al. [21]. The composting process was considered as the non-energy valorization alternative, while the energy approach was addressed according to two alternatives, from single-stage anaerobic digestion to the two-stage process combining dark fermentation with the anaerobic digestion. The treatment capacity was identical for all scenarios: 2000 t y^{-1}, considering an annual operating period of 330 d. As shown in Fig. 1, each of the facilities shares a common scheme based on feedstock pre-treatment (section SS1), biological reaction with batch operation (section SS2) and post-treatment (section SS3).

Although the post-treatment scheme depends largely on the characteristics of the current coming from the reaction section, the initial pre-treatment step has been defined common to all scenarios. This similarity can be seen in Fig. 1 but also in Fig. 2, **3** and **4**. In this sense, apple stillage from the apple bagasse distillery is fed directly to the process at 100 °C, pH 4.6 and 60% total solids as the wastewater treatment was implemented within the distillery industrial area. Therefore, temperature, solids concentration and pH were adjusted to meet the requirements of the reaction system SS2. In terms of temperature control, there are multitude types of heat exchange units for high viscous and concentrated streams, some of them reported by Peiter et al. [22] and Houdkova et al. [23].

However, based on the limitations encountered for a conceptual design from literature data, a generic heat exchange was assumed through energy balances for a first temperature reduction up to 35–70 °C (depending on the valorization alternative). In addition to energy recovery through heat exchangers, the final temperature decrease was also complemented by the direct contact transfer between streams at different temperatures in the process tank TK-101 (those needed to fulfill the dilution requirements for apple vinasses): the effluent from the post-treatment section (partial recycle) and/or additional feed water at room temperature. This activity is carried out simultaneously with pH adjustment, stillage dilution and storage in a process tank (TK-101 in Figs. 2, **3** and **4**), which also helps to buffer flow changes that may occur between the bagasse distillery and the stillage valorization facility. The pH adjustment was performed with sodium bicarbonate due to its buffering potential and minimal interference with bagasse quality. The TS concentration was reduced well below 41% in all scenarios, given that (except for Ambiogas) no commercially available technology is operating beyond this solid concentration [24].

2.1.1. *Anaerobic digestion - scenario D*

Anaerobic digestion as the single treatment of stillage, hereafter referred to as Scenario D, is the process in which the organic matter of stillage from the previous pre-treatment step would be converted into biogas (60% CH_4, 0.02% NH_3, 0.2% H_2 and 39.78% CO_2) [22]. The acidogenic, acetogenic and methanogenic stages in anaerobic digestion will be developed at mesophilic temperature (35 °C), atmospheric pressure and pH 7. Therefore, around 430 $g{\cdot}batch^{-1}$ of sodium bicarbonate was fed in the SS1 section to compensate the acidity of the vinasses.

After the SS1 section, the stillage is fed to the anaerobic reactor which is operated batchwise with a batch duration of 30 d [25]. The filling, emptying and preparation of the reactor took 24 h, 24 h and 24 h, respectively. As a result, a total of 10 batches are operated annually with a design volume of 681 m^3 (considering an additional 10% value for equipment oversizing) and a silo-type shape. The sizing of the reactor was estimated though conceptual modelling considering the annual influent flowrate and the time needed to complete the above-named batches. The supernatant from the anaerobic digestion corresponding to the liquid reactor stream is fed to the post-treatment section and then the effluent from this stage is partially recycled back to the inlet stream (i.e., SS1).

This recycled stream can be found in Fig. 2 after P-303 A/B, which is necessary for the dilution of vinasses and water savings from other sources (i.e., rivers and groundwaters). Due to this, the substrate is diluted to a TS concentration of 19.84%, which is expected to increase the biodegradability of the substrate and microbial biodiversity within the reactor [26]. Classified as dry anaerobic digestion (<25% TS) and with an initial C/N ratio of 24.4, the TS content was reduced to 10.2%.

As shown in Fig. 2, R-201 reactor is followed by a solid-liquid separation by decanting centrifuge of the digestate to obtain a cake and a filtrate, which has a concentration of 360 mg L^{-1} of TS. The filtrate is then aerobically treated at 35 °C and pH 7 in a sequential batch reactor

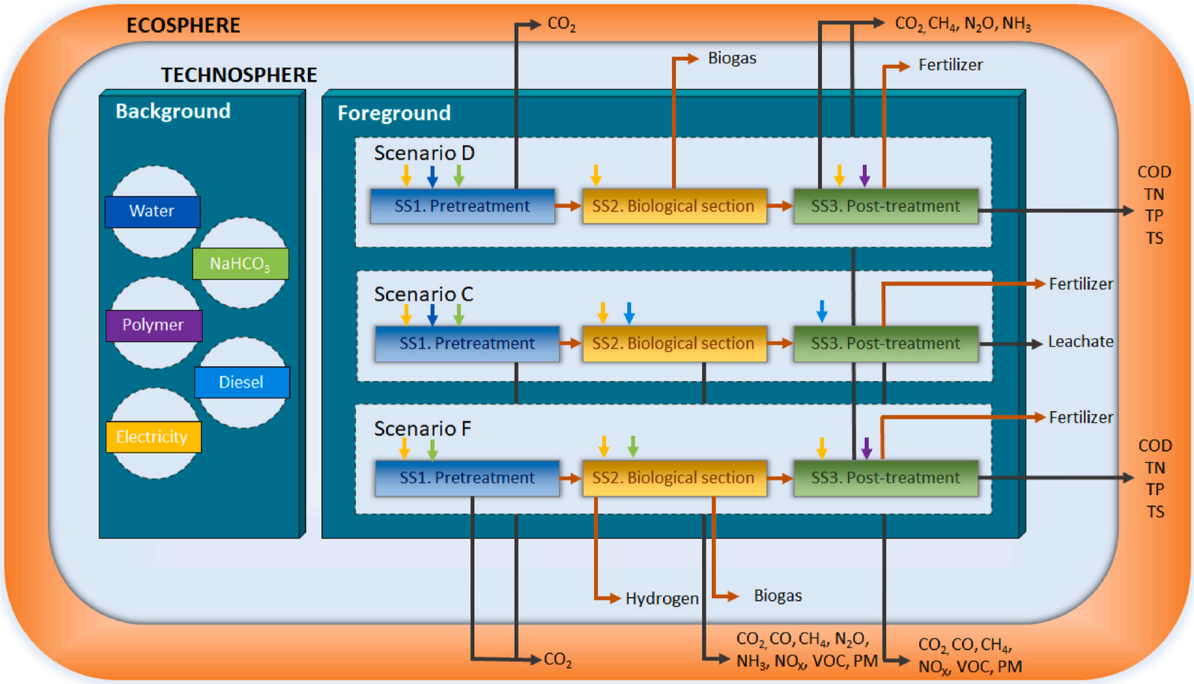

Fig. 1. Description of the system boundaries used in Life Cycle Assessment: Benchmark between scenarios. COD: Chemical Oxygen Demand; PM: Particulate matter; TN: Total Nitrogen; TP: Total phosphorus; TS: Total solids; VOC: Volatile Organic Compounds.

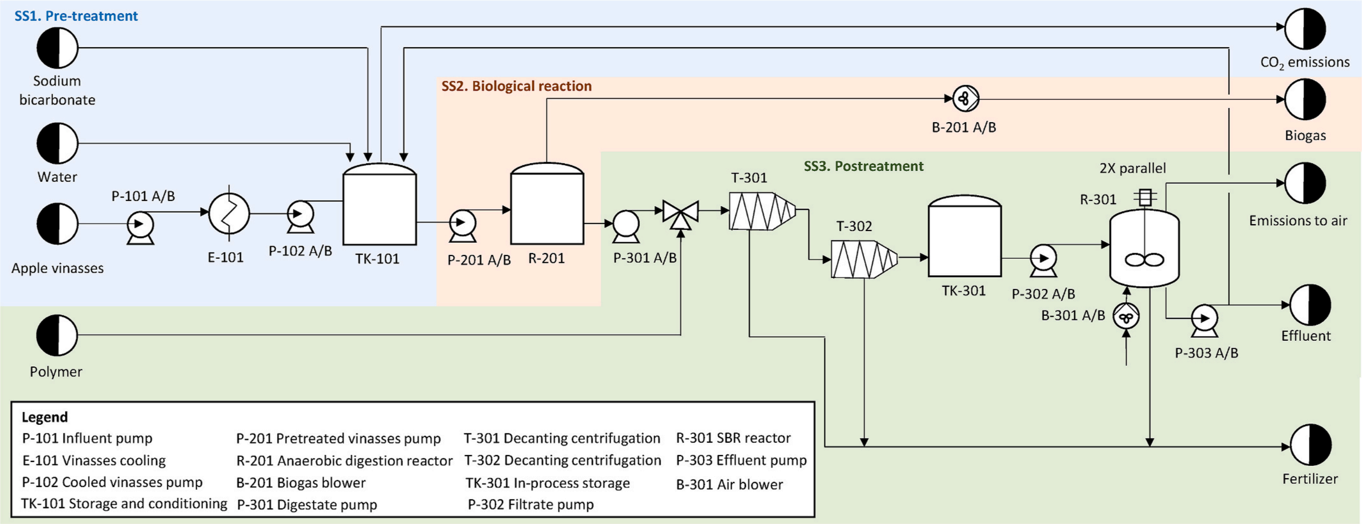

Fig. 2. Process diagram of the Scenario D (Standalone Anaerobic digestion).

(SBR) to comply with the discharge requirements for treated effluents established by European legislation [27]. On the other hand, the cake could be, together with the sludge from the SBR, used as a biofertilizer [28]. In relation to gaseous emissions, the SBR equipment also generates pollutant emissions in the form of ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2), whose contribution to different impact categories is established on the basis of the emission factors reported by Finzi et al. [29].

2.1.2. *Composting process – scenario C*

Section SS2 of the composting configuration or Scenario C was designed based on a system known as a forced individual aerated windrow for the management of a waste with a TS concentration of 40.2%, according to the recommendations of Rynk et al. [30]. Each batch of 337.9 m^3 was composted with controlled aeration and temperature of 55 °C. The volume of the pile was estimated considering the flowrate of diluted vinasses for a continuous operation of the facility, and the residence time needed to complete the aerobic degradation of the organic matter. The land surface was assumed not to be limitation and thus the time needed to create/destruct the pile was not contemplated [31]. Air was blown from inside the pile to reduce organic matter, remove excess moisture and heat with an air flow rate of 1642 $m^3\ h^{-1}$. The exhaust air stream represents the stage with gaseous emissions of water vapor, CO, CH_4, N_2O and NH_3, which were quantified according to the manuscript published by Cortés et al. [32]. The volume and characteristics of the liquid effluent were estimated from literature data reported by Čeh et al. [33] and Irka et al. [34]. The transport of compost within the facility together with the management of this stream and its treatment in a wastewater treatment plant was considered to be part of the SS3 (post-treatment) section. The schematic of scenario C is shown in Fig. 3.

2.1.3. *Dark fermentation with anaerobic digestion – scenario F*

The combined process of dark fermentation and anaerobic digestion was named Scenario F (Fig. 4) and introduces significant modifications to Scenario D described above. While the SS2 section of the facility has a treatment capacity of apple stillage with identical TS concentration for the influent and the same digestate effluent flowrate (25.4 m3·h-1), this scenario includes a two-stage digestion system for the production of biohydrogen (60.12% CO_2 and 39.88% H_2) and biogas (60% CH_4, 39.78% CO_2, 0.02% NH_3 and 0.2% H_2) separately in each unit. The effluent flowrate of the reaction system was settle considering the

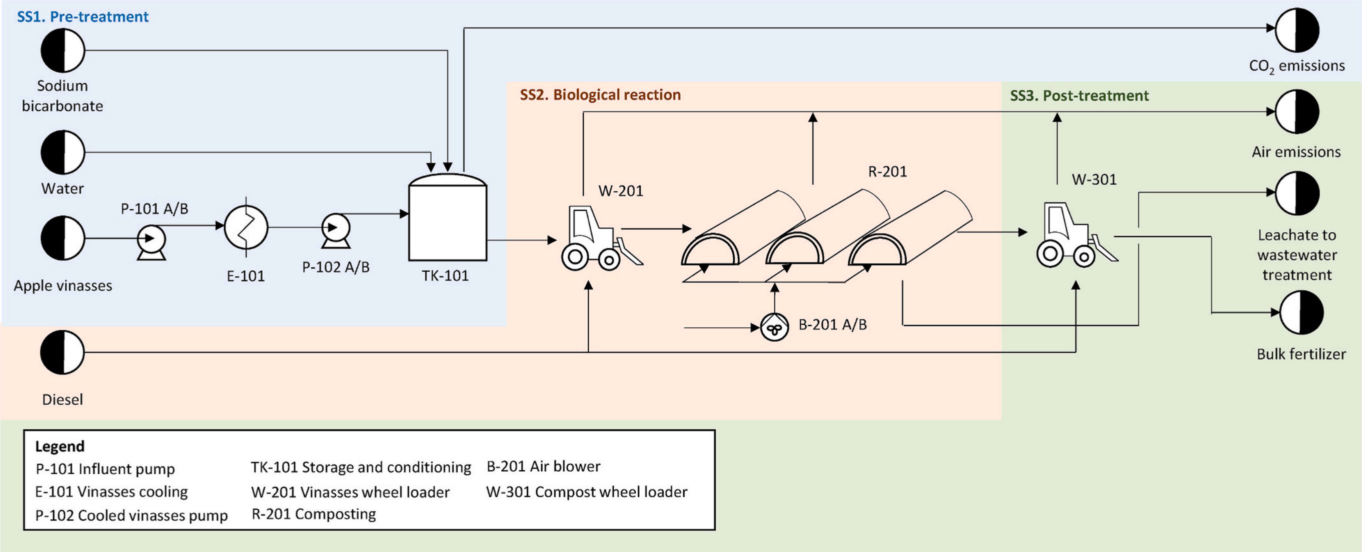

Fig. 3. Process diagram of the Scenario C (Composting).

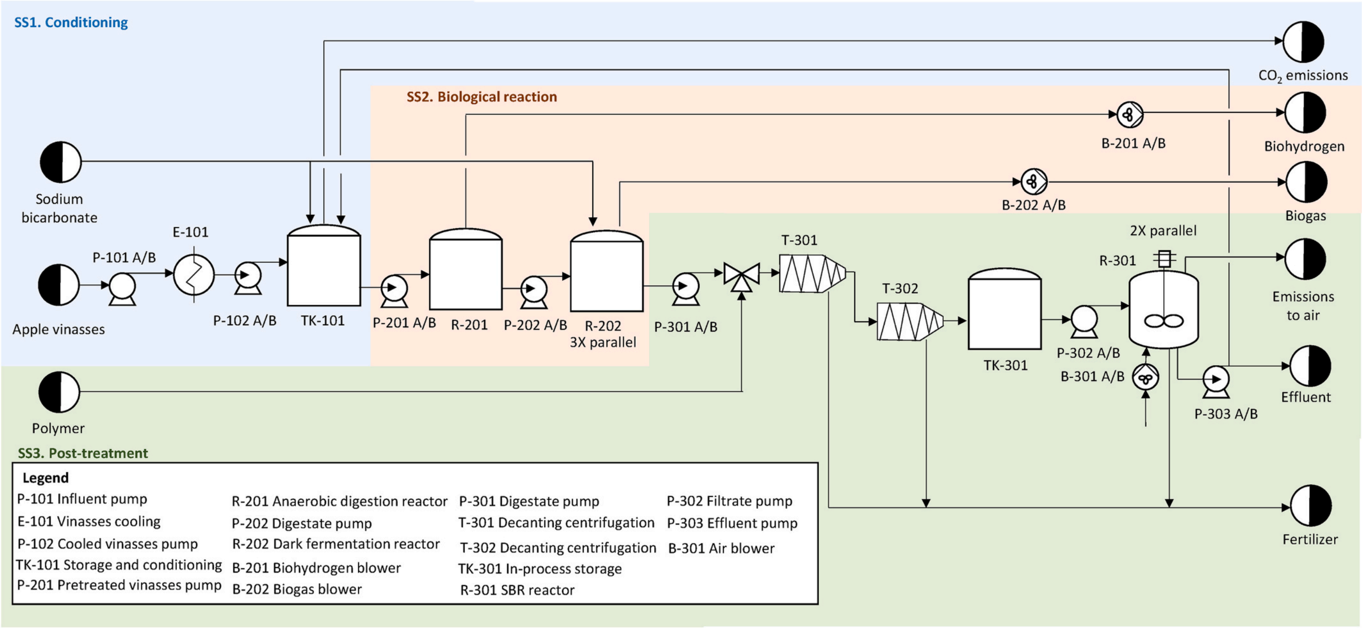

Fig. 4. Process diagram of the scenario F (Dark Fermentation with Anaerobic Digestion).

following design decisions: i) fair environmental benchmarking between processes given that the scale of the post-treatment section remains equal for both scenarios and the operational differences are only due to the effluent composition, ii) the emptying time of the reaction system, iii) the volume of the biogas producer reactor and iv) the minimum flowrate design found for commercial centrifugal thickeners (i.e., Alfa Laval, EWHA ECO SYSTEM CO., LTD.). On top of that and considering that the TS concentration ranges from 10 to 28%, the reaction scheme could be classified as solid-state dark fermentation [35].

Considering that the single-stage system has a longer hydraulic residence time (HRT) than the two-stage system (3 d), the total volume of the stage reactor and the period considered for filling (2.4 h), emptying (2.4 h) and preparation (2.4 h) differ between the two. For this reason, the total volume of reaction is 268 m^3 (four 62 m^3 reactors, one for H$_2$ production and three arranged in parallel for biogas). The reactor sizing has followed a similar procedure to the one already presented for Scenario D.

In addition, it was necessary to consider a stillage neutralization step between each step to achieve the desired optimal conditions for methanation (16.3 g·batch^{-1}). The organic matter removal efficiency was finally approximately 1–2% higher than in single-stage anaerobic digestion. For this reason, with a post-treatment operation under the same conditions, the effluent had a lower concentration of organic matter. Therefore, effluent recycling allowed that process to become more efficient with respect to water consumption (external water was no longer needed).

2.2. Assumptions and limitations

Beyond the initial evaluation assumptions, it is necessary to establish the robustness of the data according to the uncertainty analysis of the process parameters. The starting assumptions considered for the modelling of the scenarios are shown below.

(1) The energy lost though equipment walls was presumed negligible. This consideration was also extended to the piping system.
(2) The pumping energy consumption of the installation was estimated from an energy balance in which the diameter was selected according to economic criteria. On the other hand, the particle size of the stillage was assumed to be less than 200 mm. Otherwise, other transport options for the stillage should have been considered due to clogging of the equipment by particle deposits.
(3) The TK-101 storage tank is perfectly sealed and insulated and therefore emissions, such as CH$_4$ and trace volatile organic compounds, are burned and vented. This is why diffuse methane emissions were not accounted for.
(4) Carbon dioxide emissions were calculated based on a classification relative to their source origin (fossil or biogenic). This assumption was relevant when comparing biological processes since the transformation pathways of carbon compounds are different as well as the end products.
(5) Since the composting system chosen for Scenario C is not sealed, but an open process element, there is no facility to collect diffuse emissions and therefore no treatment based on biofilters, or wet scrubbers was applied for this type of emissions.
(6) Average values for air and water temperature in the surroundings were selected, so that the influence of climatic and seasonal conditions were not taken into account in the temperature variable. This assumption is especially important for the composting process, as the performance of non-reactor processes, such as windrows or static windrows, is affected by environmental conditions. In the case of the R-101 storage tank, being a closed vessel, environmental conditions in terms of temperature and precipitation do not affect the quality of the stillage.
(7) The chemicals were diluted with process (or recycled) water necessary to adjust the TS content of the stillage.
(8) Concentrations of potassium and contaminants such as heavy metals, antibiotics or siloxanes throughout the process steps were not taken into account to assess their effect on the overall mass balances, although removal rates were applied in each unit according to values reported in the literature.
(9) Inhibition by heavy and light metals, long chain volatile fatty acids, furan derivatives and phenolic compounds were not considered.
(10) Long distance emissions from truck or ship transport were not considered, as it was assumed that the bagasse and vinasse processing facilities were located within the same industrial complex (on-site waste treatment).

(11) The effects on anaerobic digestion of the oxygen concentration present in the water stream required for the dilution of the stillage were neglected.

(12) The pH was adjusted prior to the reaction mechanisms but was not controlled during the process.

(13) The viscosity of the stillage was estimated as a function of temperature as if they were 66°Brix sugarcane stillage [36]. The heat capacity was estimated on the basis of data available for malbec grape juice concentrate [37].

(14) It was assumed that the apple bagasse was properly processed to produce fermentable bioethanol so that the apple stillage was already free of metal solids and grit.

2.3. Life Cycle Assessment

2.3.1. Goal and scope definition

A benchmarking study of the environmental performance of the dark fermentation process in comparison to anaerobic digestion and composting was carried out according to the LCA methodology in accordance with ISO 14040 [38] and 14044 [39]. The system boundaries can be classified as cradle-to-gate with a zero-burden allocation for waste/recycled products (the vinasses) and for the calculation of the impacts only the operation (for both background and foreground processes) of the facility was taken into account, as these are considered central in the assessment while the construction and decommissioning phases were outside the system boundaries.

As multifunctional systems, it is necessary to consider an environmental impact allocation scheme by taking into account not only the vinasse valorization process, but also the manufacture of bioproducts such as H_2, CH_4, and fertilizers. Therefore, the selection of the functional unit (FU) is not an easy task. The subjectivity of FU preferences gives a large range of possibilities. Some of the most used in solid waste management are "per t", "per kg", "per MJ", "per $t \cdot y^{-1}$" and "per y", although there are others like "volume of hydrogen/biogas produced" and per kg of volatile solids degraded [40]. In this study, the selected FU refers to the treatment of 2000 t y^{-1}, the annual operation of the facilities of the apple stillage, following an attributional approach.

2.3.2. Life cycle inventory

The conceptual modelling of scenarios was carried out with data obtained from literature. Tables 1–3 show all data collected per functional unit for each scenario. Background processes associated with energy, chemicals and materials supply were taken from the Ecoinvent® 3.8v database [41].

2.3.3. Life cycle impact assessment

The flows from the inventory analysis were transformed into environmental contributions during this LCA stage and then impact and damage profiles were constructed for the assessed scenarios. The aim was to compare, identify hot spots and propose design strategies for better environmental performance. SimaPro® 9.3.0.2 was the software chosen to support the classification and characterization steps. ReCiPe 2016 (H) midpoint v 1.06 was the selected impact method to translate (with global characterization factors) emissions from background and foreground processes into midpoint impacts [42]. For the environmental profile, the categories assessed are global warming potential (GWP - kg CO_2-eq), terrestrial acidification (TA - kg SO_2-eq), freshwater eutrophication (FE - kg P-eq), marine eutrophication (ME - kg N-eq), land use (LU - m^2a crop-eq), fossil resource scarcity (FRS - kg oil-eq) and water consumption (WC - m^3). All of them were selected among some of the most used in the wastewater treatment sector while covering the specific needs and objectives previously named on the Introduction section [43].

The environmental consequences from the energy demand were displayed through GWP and TA, which are relevant categories for this study because of the main goal of the D and F scenarios (manufacturing of energy co-products). FE and ME are related to the emissions of TN, TP, and COD, typically measured in wastewater treatment processes to comply with legislation. LU measures the indirect impact of soil use, a category very related to the production of fertilizer given that they will be used for agricultural purposes or for soil remediation. FRS is used to conceptualize the idea that the operation of a valorization process, although it seeks to produce renewable materials from wastewater, is still dependent on the consumption of fossil resources. Finally, WC revolves around the water balance of the process. While the facility purifies the water, there is still an indirect and direct need of water for its operation.

In addition, the three endpoint indicators human health (HH), resource scarcity (RR) and ecosystem quality (EQ) are quantified through the ReCiPe 2016 (H/H) endpoint world v1.06 method [42] to obtain a single score (using normalization and weighting factors).

Table 1
LCA inventory for the apple vinasse scenario D (Standalone Anaerobic Digestion) for 2000 $t \cdot y^{-1}$ treated.

Inputs from the Technosphere			**Outputs to the Technosphere**		
Materials			**Products**		
Water	$3.47 \cdot 10^5$	kg	Biogas	80456.86	m^3
Sodium bicarbonate	4.29	kg			
Polymer	5615.99	kg	**Subproducts**		
			Fertilizer sludge	2087.36	m^3
Energy					
Pumping to heat exchanger (P-101 A/B)	1676.08	kWh	**Outputs to the nature**		
Pumping to storage tank (P-102 A/B)	7044.76	kWh	**Emissions to air from pretreatment**		
Pumping to anaerobic digester (P-201 A/B)	213.48	kWh	CO_2	565.31	kg
Pumping to thickening (P-301 A/B)	59.28	kWh	**Emissions to air from anoxic-oxic treatment**		
Thickening (T-301 and T-302)	662.77	kWh	NH_3	16.34	kg
Pumping to oxic-anoxic treatment (P-302 A/B)	0.43	kWh	N_2O	0.15	kg
Aeration in aerobic treatment (B-301 A/B)	5264.61	kWh	CO_2	12182.34	kg
Mixing in oxic treatment	1039.07	kWh	CH_4	9.53	kg
Pumping of biogas (P-303 A/B)	2064.13	kWh			
			Emissions to water		
			COD	22.88	kg
			TN	5.05	kg
			TP	$5.66 \cdot 10^{-2}$	kg
			TS	$4.64 \cdot 10^{-2}$	kg

3. Results and discussion

3.1. Environmental impact analysis (midpoint approach)

3.1.1. Environmental profile of scenario D

The environmental performance by relative contribution per section of scenario D is shown in Fig. 5a. The pre-treatment section (SS1) is the stage with the greatest influence on the profile of only two of the seven impact categories analyzed, with a total impact for LU of 45% and for WC of 65.5%. However, the post-treatment section (SS3) is the most impacting section of the scenario as it is the hotspot of the remaining five categories (GW, TA, FE, ME and FRS). In this respect, ME emerges as a category of concern with a score of around 85% for SS3. Stillage pumping from the pretreatment section and aeration from the post-treatment were the unit operations with the highest impact on the environmental profile. Their joint impacts were attributed to electricity

Table 2
LCA inventory for the apple vinasse scenario C (Composting) for 2000 $t\cdot y^{-1}$ treated.

Inputs from the Technosphere			Outputs to the Technosphere		
Materials			**Products**		
Water	$9.29\cdot10^5$	kg	Compost	905.19	t
Diesel from Wheel loader (W-201 and W-301)	42.17	kg			
Sodium bicarbonate	5.88	kg	**Outputs to the nature**		
			Emissions to air from conditioning		
Energy			CO_2	514.82	kg
Pumping to heat exchanger (P-101 A/B)	1676.08	kWh	**Emissions to air from composting**		
Pumping to storage tank (P-102 A/B)	7044.76	kWh	CO	312.46	kg
Aeration of the pile (B-201 A/B)	102055.28	kWh	CH_4	3362.16	kg
			N_2O	837.45	kg
			NH_3	837.45	kg
			Emissions to air from loader		
			CO	0.34	kg
			CH_4	0.01	kg
			NO_x	1.61	kg
			CO_2	157.03	kg
			VOC	$7.84\cdot10^{-2}$	kg
			PM	$4.02\cdot10^{-2}$	kg
			Waste		
			Wastewater treatment		
			Leachate	27.88	m^3

Table 3
LCA inventory for the apple vinasse scenario F (Dark Fermentation with Anaerobic Digestion) for 2000 $t\cdot y^{-1}$ treated.

Inputs from the Technosphere			Outputs to the Technosphere		
Materials			**Products**		
Sodium bicarbonate	4.29	kg	Biohydrogen	53762.10	m^3
Polymer	4627.90	kg	Biogas	88085.80	m^3
			Subproducts		
Energy			Fertilizer sludge	1698.58	m^3
Pumping to heat exchanger (P-101 A/B)	1676.08	kWh			
Pumping to storage tank (P-102 A/B)	7824.67	kWh	**Outputs to the nature**		
Pumping to dark fermentation reactor (P-201 A/B)	214.19	kWh	**Emissions from pretreatment**		
Pumping to anaerobic digester (P-202 A/B)	214.19	kWh	CO_2	565.31	kg
Pumping to thickening (P-301 A/B)	53.55	kWh	**Emissions from anoxic-oxic treatment**		
Thickening (T-301 and T-302)	643.32	kWh	NH_3	17.70	kg
Pumping to oxic-anoxic treatment (P-302 A/B)	0.58	kWh	N_2O	0.16	kg
Aeration in aerobic treatment (B-301 A/B)	5264.61	kWh	CO_2	8512.59	kg
Mixing in oxic treatment	1039.07	kWh	CH_4	10.32	kg
Pumping of biohydrogen (B-201 A/B)	0.58	kWh			
Pumping of biogas (B-202 A/B)	2259.85	kWh	**Emissions to water**		
			COD	16.68	kg
			TN	5.25	kg
			TP	$5.89\cdot10^{-2}$	kg
			TS	$3.93\cdot10^{-2}$	kg

consumption with rated results being in the range of 9.3–35.1% (GWP and LU), respectively.

Indeed, as shown in Fig. 6, energy use in scenario D showed a strong effect on the environment in four impact categories (FE, LU, FRS, and WC). A share of more than 91% was identified with respect to the total estimated score for the LU category. On the other hand, direct emissions from process operation had a significant effect on the GWP and ME categories. In this respect, the CO_2, CH_4 and N_2O components are the main contributors to the GW profile with about 47% of the impacts. Biogenic carbon dioxide emissions accounted for about 97% of the total carbon emissions, which should be considered if the process can be compared to technologies relying on non-biological resources. Otherwise, marine eutrophication was influenced by aqueous emissions mainly related to total nitrogen with a contribution of 72%.

In addition to energy and direct emissions, the consumption of chemicals at the facility: sodium bicarbonate for pH control and polymers for thickening, presented a large contribution to environmental impacts and considering a joint contribution, percentages around 66% (related to FRS) were reached, which was mainly attributed due to the demand for polymers.

3.1.2. *Environmental profile of scenario C*

In contrast to Scenario D, the environmental profile of scenario C is mainly defined by section SS2 (biological reaction) except for the WC category, being representative in almost all categories from 87% (in ME) to 99.9% (in GWP) (shown in Fig. 5b). Windrow aeration and direct emissions from composting and the use of wheel loaders are operations that represent significant impacts. While the former represents a key role in impact categories such as FE, ME, LU, FRS and WC, direct gaseous emissions became relevant for GWP and TA loads (99% and 92%, respectively). Therefore, the profile is dominated by electricity demand in the air blower (for an average pile flow rate of 4.86 $m^3\ h^{-1}\ m^{-3}$) and by carbon dioxide emissions (88.1% gaseous emission during composting, 99.99% biogenic). Therefore, the background system is mainly controlled by energy consumption while chemical demand is negligible in comparison (below 0.1%, in all categories).

3.1.3. *Environmental profile of scenario F*

The environmental profile of Scenario F is similar to that obtained by Scenario D, as shown in Fig. 5c. The dark fermentation process followed by anaerobic digestion was characterized by very similar values of the impacts on the SS1 section (12–45% in scenario D and 15–43% in scenario F). Although we cannot identify a significant change, the viscosity of the stillage and how that parameter affects the energy needs for pumping do vary. Although the temperature in both scenarios corresponds to the mesophilic range (35 °C), scenario D is complemented by an external water at a much lower temperature. On the other hand, the involvement of SS1 in the environmental profile has been mitigated by a decrease in chemical demand to adjust the initial pH. In this scenario, dark fermentation operates at a lower pH than single-step anaerobic digestion. However, the reduction is only represented by 0.03–0.20% of the total impact generated by the section (compared to 0.05–0.34% for scenario D).

However, the relevance of the environmental impacts in section SS3 has decreased by values that can represent an improvement of up to 7.5% (WC). The difference between the two scenarios is mainly due to polymer consumption during the thickening stage. In this sense, the removal of volatile solids in the two-stage system was considered 12% higher and therefore the solid load in the decanter centrifuge was 19% lower.

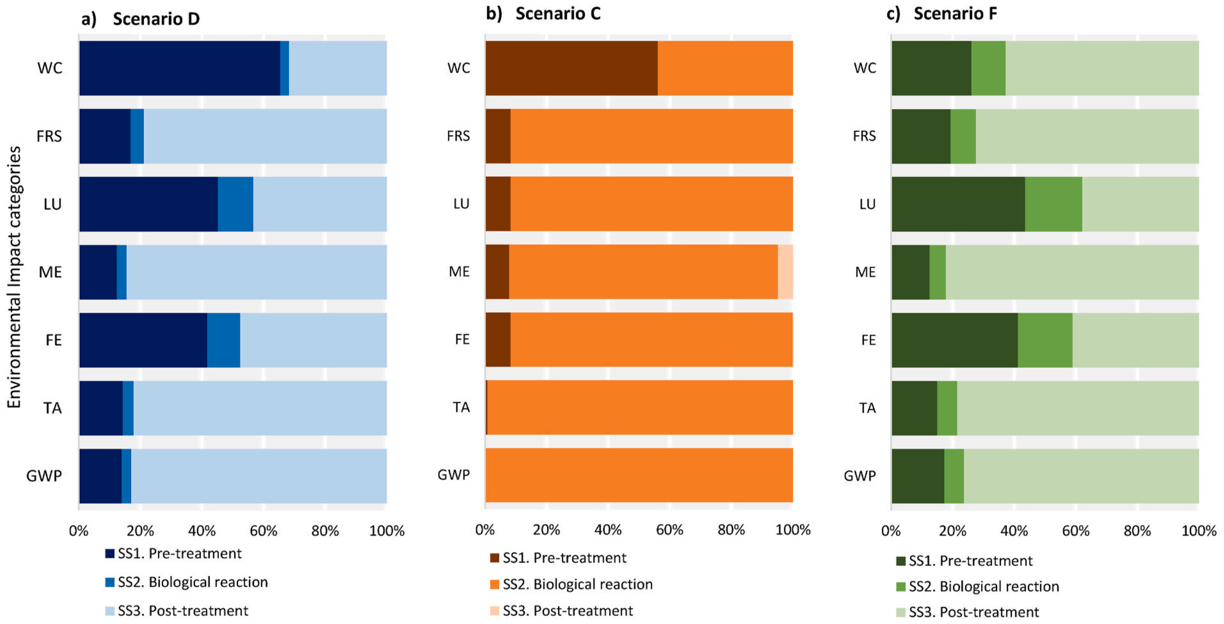

Fig. 5. Relative environmental profile for (a) scenario D, (b) scenario C and (c) scenario F. Scenario D: Standalone Anaerobic Digestion; Scenario C: Composting; Scenario F: Dark Fermentation with Anaerobic Digestion; GWP: Global Warming Potential; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; LU: Land Use; FRS: Fossil Resource Scarcity and WC: Water consumption.

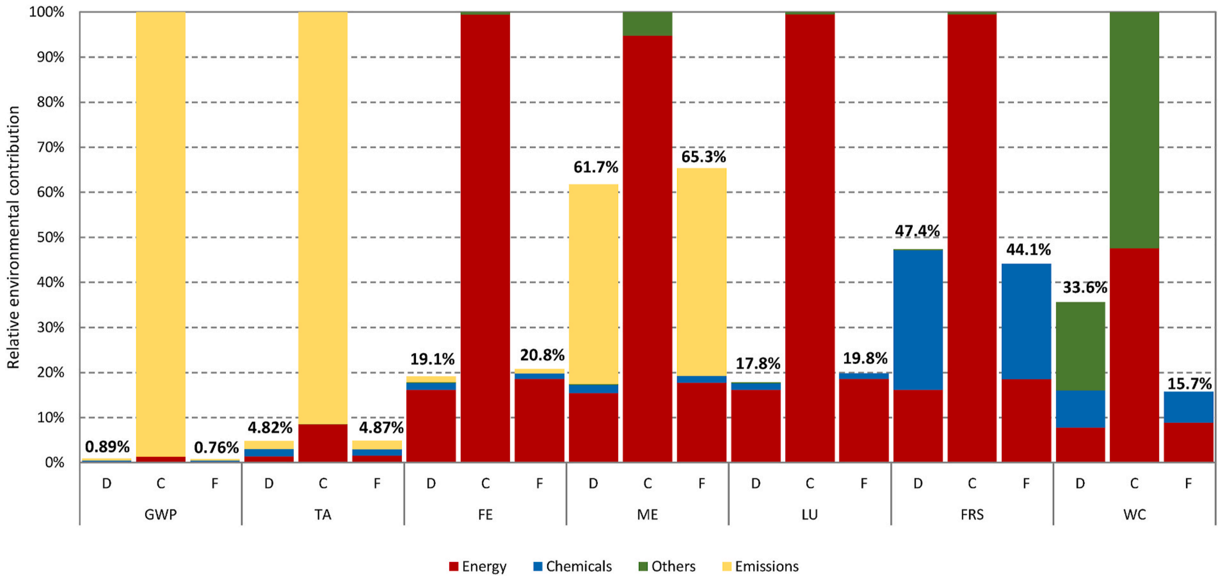

Fig. 6. Midpoint relative environmental profile for each scenario subdivided by source of impact. D: Standalone Anaerobic Digestion scenario; C: Composting scenario; F: Dark Fermentation with Anaerobic Digestion scenario; GWP: Global Warming Potential; TA: Terrestrial Acidification; FE: Freshwater Eutrophication; ME: Marine Eutrophication; LU: Land Use; FRS: Fossil Resource Scarcity and WC: Water consumption.

3.2. Environmental damage analysis (endpoint approach)

3.2.1. Environmental profile of scenario D

In this section the environmental results are expressed as damage categories and translated into a single overall score (see Fig. 7). In contrast to the results obtained with the mid-point approach, the endpoint analysis of the environmental cause-effect chain appeared to be defined mainly by direct emissions (42%). However, good energy management of the process also opens the possibility to improve the endpoint profile since about 24% of the damage comes from energy demand. On the other hand, and despite the low contribution (19 Pt out of 421 Pt) of the RR category to the single score, a relative share for energy of 19% was found in this category. In terms of the individualized contribution of the different sections, section SS3 was the most environmentally damaging (80% of the total score compared to 17% for SS1 and 3% for SS2).

3.2.2. Environmental profile of scenario C

The environmental profile of scenario C in the endpoint perspective (shown in Fig. 7) presents the relevance of the HH damage category (around 88%) and direct emissions (99%). In contrast, RR (0.05%) and HH (12%) did not represent a significant contribution to the overall score compared to HH.

The hotspot of the process was found in the biological reaction section (SS2), which accounted for about 99.8% of the overall damage score. The damage created by stillage transport and stack aeration was

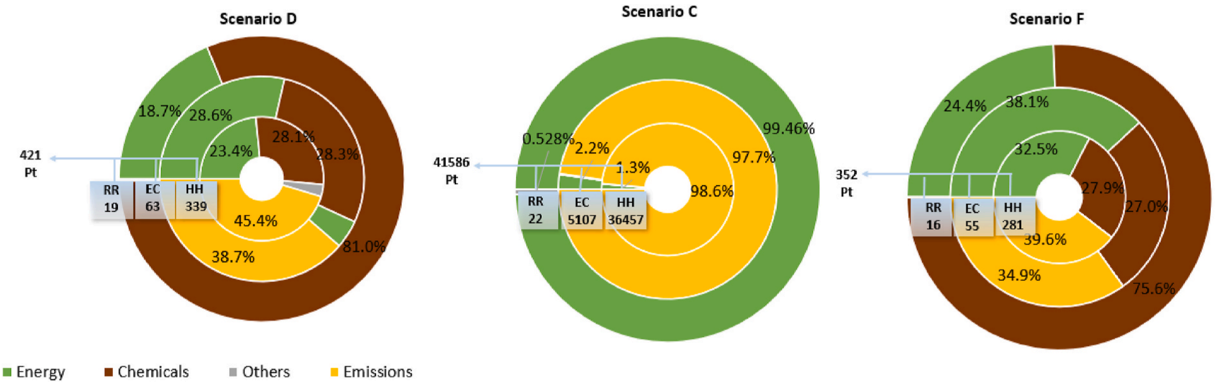

Fig. 7. Endpoint damage profile for each scenario and type of contributing source (energy, chemicals, direct emissions, or others). Scenario D: Standalone Anaerobic Digestion; Scenario C: Composting; Scenario F: Dark Fermentation with Anaerobic Digestion; RR: Resources; HH: Human Health; EC: Ecosystems.

only 2%, while the largest impact came from direct emissions from the stack, with CO_2 (87%) and N_2O (8%) being the most important contributions.

3.2.3. Environmental profile of scenario F

The environmental profile of scenario F is similar to scenario D (see Fig. 7), with damage from direct emissions being the distinguishing feature (37%). While chemicals account for 30.4% of the profile of scenario D, the contribution of this utility for scenario F is slightly smaller (30%). In both cases, RR was the category that best identified the chemical effect on the environmental damage profile (81% and 76% for scenarios D and F, respectively). In addition to chemicals, the contribution of direct emissions also decreases from scenario D to F (42%–37%). The reason behind this change comes from the organic matter yield in the reaction system (the two-stage process was more efficient), which translates into reduced carbon dioxide and COD emissions from the oxic-anoxic treatment of the SS3 section (30% and 27% for each).

According to the midpoint results, it could also be noted that the overall score achieved in the endpoint analysis also showed an increase in representativeness for section SS1 (from 14% to 17%) and a decrease for SS3 (83%–76%).

3.3. Scenario and literature benchmarking

Once the different scenarios have been analyzed with various perspectives, the next step is the identification of the most advisable option from an environmental point of view. Although scenario D is the most competitive in four (TA, FE, ME and LU) of the seven categories analyzed (see Fig. 6), the differences between D and F can be considered minor or irrelevant compared to scenario C (they represent a 0.89% and 0.76% of the total impact of C in GWP, respectively). On the other hand, the disparity between the results of the two scenarios between each other is no more than 11% (value for LU), except for GWP and WC (14.6% and 55.7% that seems to advocate for scenario F as a better option). In this regard, the inequality between results and categories and be arranged from large to minor as WC, GWP, LU, FE, FRS, ME, and TA. Considering a better performance in a greater number of categories, scenario D seems to provide a preferable profile. However, and taking into account the larger difference for GWP and WC, the selected valorization strategy should be F. This small difference is similar when the D and F scenarios were compared with the single score achieved by the endpoint analysis (see Fig. 7), so that the dark fermentation scenario is the most favorable with a difference of 16%. This is aligned with the technical improvement value for a two-stage system stated by Cremonez et al. [44] (around 13% improvement in VS degradation). Moreover, operational advantages have been identified in terms of operating flexibility and reactor size [44]. Although it seems that the direction of the results is encouraging the implementation of scenario F instead of D, the truth is that the difference between their profiles is not large enough to lean towards one of them. One of the reasons behind this could be the stability during the operation of biological processes. For example, Castelló et al. [45] has stated the potential problems and solutions for this issue in the dark fermentation process. The metabolic diversity of the microorganism's population, inhibitory compounds, and fluid dynamics are some tougher factors to be implemented in a modeled process while they bring instability to the valorization treatment. Thus, LCA and design assumptions may lead to a drastic change in the environmental profile. Barrera et al. [46] studied the environmental performance of lagoon treatment systems for vinasses and compared the results with those retrieved from 18 alternatives for an anaerobic digestion scenario (with and without dilution of vinasses and considering biogas transformation to electricity with several engines). Although anaerobic digestion was favored with an average 77% (endpoint) reduction in the profile compared to lagooning, the difference observed between the results of anaerobic digestion alternatives reached about 15% [46]. Apart from this, Patterson et al. [47] reached similar findings for the valorization of wheat feed. They have reported larger benefits for dark fermentation when improving the process efficiency (i.e., with an increase of organic feed) and, thus, enhancing the energy outcomes as biohydrogen/biogas. If that is not the case, anaerobic digestion would give the best environmental profile [47]. Therefore, and although the research for dark fermentation seems to be going into the right direction to reduce the environmental profile compared to the technologies of D [47], the actual situation is that the dissimilarity between them is not large enough to opt for one technology (dark fermentation) instead of the other (anaerobic digestion). The selection should be focused instead on the type of products provided to fulfill market needs and socio-economic assessments.

On the other hand, scenario C does appear to be the most unfavorable in all midpoint and endpoint categories with a difference of 99% compared to scenario D (see Figs. 6 and 7). The comparison highlights the divergences found for two key elements: energy consumption and direct emissions. The aerobic degradation of organic matter, which is transformed into carbon dioxide, is related to a higher energy demand of the blower for oxygen supply and the associated environmental impacts on emissions. Despite being primary biogenic, Fig. 6 shows, for the GWP category, how scenario D has lower direct emissions than C from stillage treatment (in all cases with the same composition). For this reason, and regardless of whether they are operated with or without oxygen deficiency, composting processes are penalized for not being able to recover organic matter as a valuable resource.

Although not for vinasses, similar results were obtained from Behrooznia et al. [48] for composting when compared to anaerobic digestion. In this instance, the treatment of 100 t of municipal solid wastes lead to a reduction of 89.64% for the GWP (midpoint) and a 99.66% for a single score retrieved from the weighting of endpoint categories. As in this study, direct emission and energy were the main hotspots. The former mostly affected human health and climate change, whereas electricity and diesel were relevant for the category of resources [48]. The outperformance of the anaerobic digestion system was also demonstrated by Edwards et al. [49] whose study showed better achievement in six out of eight categories compared to composting. Although only first ranked in GWP, FRS and TA in relationship to the seven technologies considered by Edwards et al. [49], it showed steadiness in the conclusions achieved for the GWP given that the uncertainty analysis confirmed 95% of the trials.

Other alternatives/technologies have been analyzed with LCA for stillage such as conventional fertigation, concentration-fertigation and concentration-incineration. However, biological systems such as anaerobic digestion were not shown to be as competitive as the others. For example, the research performed by Silva Lora et al. [50] has only advocated for anaerobic digestion in one (abiotic depletion potential) out of the nine impact categories they have analyzed, and the outcomes led to a better performance of direct fertigation before the concentration of the stillage [50]. This is in line with the statements of Mayer et al. [51], which claimed in their study that same technological comparisons have drawn conclusions with different tendencies (i.e., the discussion about the performance of incineration and anaerobic digestion) and was driven in some cases by the substrate characteristics, such as moisture content [51].

Returning back to the benchmarking of scenario F with the results from other studies for stillage valorization, it seems to be limitations from an LCA perspective not related to technological (design of systems) or methodological (system boundaries and functional unit among others) factors but rather to the combination of the valorization system (dark fermentation) and the selected substrate. The research of Camacho et al. [52] can be highlight as an example of dark fermentation treatment and valorization of a mixture of wine vinasse with sewage sludge, however, the goal was the extraction of information related to the environmental viability of substrate, instead of technology benchmarking.

Considering the substrate as uncertainty variable for the environmental performance of dark fermentation, the results comparison can also be made in relation to literature studies evaluating the different feedstocks. Thus, to analyze the results obtained focusing on the GWP category and scenario F, the impacts were recorded per kg H_2 too. In this regard, GWP is then 0.152 kg CO_2eq, considering a volume allocation approach (with an allocation factor of 37% for H_2). For example, Wulf and Kaltschmitt [53] obtained a range of GHG emissions of about 3.5 and 15.3 kg CO_2eq per kg H_2 for a cradle-to-grave analysis based on woody and herbaceous biomass, energy crops and organic by-products, among others. Furthermore, Djomo and Blumberga [54] followed a "well-to-tank" boundary (i.e., H_2 combustion in the vehicle was not considered) and reported that GHG emissions ranged from 5.2 to 5.6 kg CO_2eq per kg H_2 from sweet sorghum stalk and wheat straw, respectively. Impacts related to the GWP category were caused by the flaring of natural gas for electricity production. The study of Manish and Banerjee [55] reported a GWP value of 3.4 kg CO_2 per kg H_2 for a two-stage bioprocess fed with sugar cane. In their definition of limits, they did not include gas treatment and compression as well as storage processes (similar to this study). In this regard, when Djomo and Blumberga [54] excluded the aforementioned stages, they obtained a GWP value close to Manish and Banerjee [55] of approximately 3.04 kg CO_2 kg per kg H_2. This highlights the relevance of boundary definition in comparing profiles of technology alternatives. In a recently published paper, Reaño [56] is the only study to perform a gate-to-gate environmental analysis to compare six biohydrogen production processes. The dark fermentation scenarios using a cogeneration system (CHP) and fossil fuels obtain a close GWP profile of approximately 10.9 kg CO_2eq per kg H_2 gas. The main sources of emissions were related to rice husk processing for the CHP system and diesel for electricity production, respectively. Furthermore, this approach only yields H_2 as an end product (with solid waste as a by-product and related emissions). In this sense, the coupling of dark fermentation with anaerobic digestion seems to represent an efficient alternative from a multi-product perspective (H_2 and biogas obtained as main products), which also benefits the environmental profile of H_2 production (due to allocation loads).

4. Conclusions

This study has presented an environmental comparison of three strategies for the management of apple stillage from bioethanol processing: composting, anaerobic digestion and dark fermentation as pretreatment of anaerobic digestion. In the midpoint perspective, standalone anaerobic digestion stands out as the most competitive strategy but with a marginal difference (up to 15% and 58% for GWP and WC, much lower for other categories) to the combined dark fermentation-anaerobic digestion scenario. However, from an end-point approach, the latter scenario represents the most environmentally friendly alternative with a larger gap against anaerobic digestion (16%).

An analysis of the contributing impacts in an endpoint methodology identifies direct emissions as the main contributor to the impacts, although energy consumption was highlighted as the main contributor in the midpoint approach. The balance identified in both the comparative scenario assessment and the scenario hotspots reflects the relevance of conducting a joint environmental analysis of impact and harm to analyze one or the other option in detail before the final decision-making process. A complementary analysis based on field data would allow validation of the results obtained, but this analysis requires a prior critical review of the processes proposed, so as to discard those that clearly do not point in a sustainable direction. This is why the importance of this type of analysis is becoming increasingly important. It is preferable to propose a multi-criteria analysis approach that includes process modelling and analysis of environmental impacts for a technology under development than to operate non-optimized systems in which a previous analysis could have provided hints for improvement.

Credit author statement

Sofía Estévez: Methodology, formal analysis, investigation, writing - original draft, visualization, **Ricardo Rebolledo-Leiva**: Conceptualization, validation, writing - original draft, **Diógenes Hernández:** Investigation, validation, writing – Review, **Sara González-García:** Validation, writing - Review & Editing, supervision, **María Teresa Moreira:** Validation, writing - Review & Editing, supervision, **Gumersindo Feijoo:** Validation, writing - review & editing, supervision.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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References

[1] Bušić A, Marđetko N, Kundas S, Morzak G, Belskaya H, Šantek MI, et al. Bioethanol production from renewable raw materials and its separation and purification: a review. Food Technol Biotechnol 2018;56:289–311. https://doi.org/10.17113/ftb.56.03.18.5546.

[2] Formann S, Hahn A, Janke L, Stinner W, Sträuber H, Logroño W, et al. Beyond sugar and ethanol production: value generation opportunities through sugarcane residues. Front Energy Res 2020;8:579567. https://doi.org/10.3389/fenrg.2020.579577.

[3] Montiel-Rosales A, Montalvo-Romero N, Enrique García-Santamaría L, Carlos Sandoval-Herazo L, Bautista-Santos H, Fernández-Lambert G. Post-industrial use of sugarcane ethanol vinasse: a systematic review. Sustainability 2022;14:11635. https://doi.org/10.3390/su141811635.

[4] Alavi N, Daneshpajou M, Shirmardi M, Goudarzi G, Neisi A, Babaei AA. Investigating the efficiency of co-composting and vermicomposting of vinasse with the mixture of cow manure wastes, bagasse, and natural zeolite. Waste Manag 2017;69:117–26. https://doi.org/10.1016/J.WASMAN.2017.07.039.

[5] Ferraz P, Amorim-Rodrigues M, Cassio F, Lucas C. Vinasse waste from sugarcane-based bioethanol production plants kills Moniliophthora Perniciosa, the causative agent of Cacao witches' broom disease. Ann. Agric. Crop Sci. 2021;6:1073. https://doi.org/10.26420/annagriccropsci.2021.1073.

[6] Robles-González V, Galíndez-Mayer J, Rinderknecht-Seijas N, Poggi-Varaldo HM. Treatment of mezcal vinasses: a review. J Biotechnol 2012;157:524–46. https://doi.org/10.1016/J.JBIOTEC.2011.09.006.

[7] Madejón E, López R, Murillo JM, Cabrera F. Agricultural use of three (sugar-beet) vinasse composts: effect on crops and chemical properties of a Cambisol soil in the Guadalquivir river valley (SW Spain). Agric Ecosyst Environ 2001;84:55–65. https://doi.org/10.1016/S0167-8809(00)00191-2.

[8] Hoarau J, Caro Y, Grondin I, Petit T. Sugarcane vinasse processing: toward a status shift from waste to valuable resource. A review. J Water Proc Eng 2018;24:11–25. https://doi.org/10.1016/J.JWPE.2018.05.003.

[9] Harirchi S, Wainaina S, Sar T, Nojoumi SA, Parchami M, Parchami M, et al. Microbiological insights into anaerobic digestion for biogas, hydrogen or volatile fatty acids (VFAs): a review. Bioengineered 2022;13:6521–57. https://doi.org/10.1080/21655979.2022.2035986.

[10] Lin L, Xu F, Ge X, Li Y. Improving the sustainability of organic waste management practices in the food-energy-water nexus: a comparative review of anaerobic digestion and composting. Renew Sustain Energy Rev 2018;89:151–67. https://doi.org/10.1016/j.rser.2018.03.025.

[11] Younesian M, Cheraghi M, Sobhanardakani S, Lorestani B, Merrikhpour H. Assessment of the differences between composting and anaerobic digestion of sludge. Arabian J Geosci 2021;14. https://doi.org/10.1007/s12517-021-08891-6.

[12] Eurostat. Energy - overview. Https://EcEuropaEu/Eurostat/Web/Energy/Overview; 2022.

[13] Jens J, Gräf D, Schimmel M. A Gas for Climate report Market state and trends in renewable and low-carbon gases in Europe December 2021. 2021.

[14] Patel SKS, Lee J-K, Kalia VC. Beyond the theoretical yields of dark-fermentative biohydrogen. Indian J Microbiol 2018;58:529–30. https://doi.org/10.1007/s12088-018-0759-4.

[15] Albini E, Pecorini I, Ferrara G. Improvement of digestate stability using dark fermentation and anaerobic digestion processes. Energies 2019;12:3552. https://doi.org/10.3390/en12183552.

[16] Cavinato C, Giuliano A, Bolzonella D, Pavan P, Cecchi F. Bio-hythane production from food waste by dark fermentation coupled with anaerobic digestion process: a long-term pilot scale experience. Int J Hydrogen Energy 2012;37:11549–55. https://doi.org/10.1016/J.IJHYDENE.2012.03.065.

[17] Schievano A, Pepé Sciarria T, Gao YC, Scaglia B, Salati S, Zanardo M, et al. Dark fermentation, anaerobic digestion and microbial fuel cells: an integrated system to valorize swine manure and rice bran. Waste Manag 2016;56:519–29. https://doi.org/10.1016/j.wasman.2016.07.001.

[18] Masilela P, Pradhan A. Systematic literature review of the sustainability and environmental performance of dark fermentative biohydrogen production. J Clean Prod 2022;372:133541. https://doi.org/10.1016/J.JCLEPRO.2022.133541.

[19] Molinuevo-Salces B, Riaño B, Hijosa-Valsero M, González-García I, Paniagua-García AI, Hernández D, et al. Valorization of apple pomaces for biofuel production: a biorefinery approach. Biomass Bioenergy 2020;142:105785. https://doi.org/10.1016/J.BIOMBIOE.2020.105785.

[20] Rusecki H, Skowronska M, Chojnacka S, Kraska P, Andruszczak S, Mocek-Płóciniak A. Fertilizing potential of rye stillage in a maize agroecosystem. Agronomy 2019;9. https://doi.org/10.3390/agronomy9110688.

[21] Hernández D, Rebolledo-Leiva R, Fernández-Puratich H, Quinteros-Lama H, Cataldo F, Muñoz E, et al. Recovering apple agro-industrial waste for bioethanol and vinasse joint production: screening the potential of Chile. Fermentation 2021;7:203. https://doi.org/10.3390/fermentation7040203.

[22] Peiter FS, Hankins NP, Pires EC. Evaluation of concentration technologies in the design of biorefineries for the recovery of resources from vinasse. Water Res 2019;157:483–97. https://doi.org/10.1016/J.WATRES.2019.04.003.

[23] Houdkova L, Boran J, Elsäßer T, Stehlik P. Importance of experimental measurements and simulations for \“sludge-to-energy” systems. WIT Trans Modelling Simul 2007;46:10. https://doi.org/10.2495/CMEM070471.

[24] André L, Pauss A, Ribeiro T. Solid anaerobic digestion: state-of-art, scientific and technological hurdles. Bioresour Technol 2018;247:1027–37. https://doi.org/10.1016/j.biortech.2017.09.003.

[25] Riya S, Meng L, Wang Y, Lee CG, Zhou S, Toyota K, et al. Dry anaerobic digestion for agricultural waste recycling. Biogas - Recent advances and integrated approaches; 2020.

[26] Harihastuti N, Yuliasri R, Djayanti S, Handayani NI, Rame R, Prasetio A, et al. Full-scale application of up-flow high rate anaerobic reactor with substrate modification and effluent recirculation for sugarcane vinasse degradation and biogas generation. J Ecol Eng 2022;22:314–24. https://doi.org/10.12911/22998993/134036.

[27] Eur-Lex. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. 2014.

[28] Tambone F, Valentina Orzi V, D'Imporzano G, Adani F. Solid and liquid fractionation of digestate: mass balance, chemical characterization, and agronomic and environmental value. Bioresour Technol 2017;243:1251–6. https://doi.org/10.1016/j.biortech.2017.07.130.

[29] Finzi A, Mattachini G, Lovarelli D, Riva E, Provolo G. Technical, economic, and environmental assessment of a collective integrated treatment system for energy recovery and nutrient removal from livestock manure. Sustainability 2020;12:2756. https://doi.org/10.3390/su12072756.

[30] Rynk R, Black G, Biala J, Bonhotal J, Cooperband L, Gilbert J, et al. The composting handbook: a how-to and why manual for farm, municipal. Institutional and commercial composters, vol. 1. Elsevier; 2022. https://doi.org/10.1016/C2019-0-05417-9.

[31] Lalremruati M, Devi AS. Duration of composting and changes in temperature, pH and C/N ratio during composting: a review. Agric Rev 2021. https://doi.org/10.18805/ag.r-2197.

[32] Cortés A, Oliveira LFS, Ferrari V, Taffarel SR, Feijoo G, Moreira MT. Environmental assessment of viticulture waste valorisation through composting as a biofertilisation strategy for cereal and fruit crops. Environ Pollut 2020;264:114794. https://doi.org/10.1016/J.ENVPOL.2020.114794.

[33] čeh B, Luskar L, Hladnik A, Trošt Ž, Polanšek J, Naglič B. The quantity and composition of leachate from hop plant biomass during composting process. Appl Sci 2022;12:2375. https://doi.org/10.3390/app12052375.

[34] Ibrahim Irka C, Prudent P, Théraulaz F, Farnet Da Silva A-M, Asia L, Gori D, et al. Treatment of sewage sludge compost leachates on a green waste biopile: a case study for an on-site application. Processes 2022;10:1196. https://doi.org/10.3390/pr10061196.

[35] Tapia-Venegas E, Ramirez-Morales JE, Silva-Illanes F, Toledo-Alarcón J, Paillet F, Renaud E, et al. Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. Rev Environ Sci Biotechnol 2015;14:761–85. https://doi.org/10.1007/s11157-015-9383-5.

[36] Brossard Perez LE, Bezzon G, Olivares Gómez E. Use of a rotational bench viscometer to study the influence of temperature and agitation speed on vinasse viscosity. Braz J Chem Eng 2000;17:133–41.

[37] Evangelista RR, Sanches MAR, de Castilhos MBM, Cantú-Lozano D, Telis-Romero J. Determination of the rheological behavior and thermophysical properties of malbec grape juice concentrates (Vitis vinifera). Food Res Int 2020;137. https://doi.org/10.1016/j.foodres.2020.109431.

[38] EN ISO 14040. Environmental management — life cycle assessment — principles and framework. 2006. 2006.

[39] ISO., ISO. Life cycle assessment — requirements and guidelines. 2006, 14044.

[40] Mulya KS, Zhou J, Phuang ZX, Laner D, Woon KS. A systematic review of life cycle assessment of solid waste management: methodological trends and prospects. Sci Total Environ 2022:831. https://doi.org/10.1016/j.scitotenv.2022.154903.

[41] Wernet G, Bauer C, Steubing B, Reinhard J, Moreno-Ruiz E, Weidema B. The ecoinvent database version 3 (part I): overview and methodology. Int J Life Cycle Assess 2016;21:1218–30. https://doi.org/10.1007/s11367-016-1087-8.

[42] Huijbregts MAJ, Steinmann ZJN, Elshout PMF, Stam G, Verones F, Vieira M, et al. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int J Life Cycle Assess 2017;22:138–47. https://doi.org/10.1007/s11367-016-1246-y.

[43] Mehmeti A, Canaj K. Environmental assessment of wastewater treatment and reuse for irrigation: a mini-review of LCA studies. Resources 2022;11. https://doi.org/10.3390/resources11100094.

[44] Cremonez PA, Teleken JG, Weiser Meier TR, Alves HJ. Two-Stage anaerobic digestion in agroindustrial waste treatment: a review. J Environ Manag 2021;281:111854. https://doi.org/10.1016/J.JENVMAN.2020.111854.

[45] Castelló E, Nunes Ferraz-Junior AD, Andreani C, Anzola-Rojas M del P, Borzacconi L, Buitrón G, et al. Stability problems in the hydrogen production by dark fermentation: possible causes and solutions. Renew Sustain Energy Rev 2020;119. https://doi.org/10.1016/j.rser.2019.109602.

[46] Barrera EL, Rosa E, Spanjers H, Romero O, De Meester S, Dewulf J. A comparative assessment of anaerobic digestion power plants as alternative to lagoons for vinasse treatment: life cycle assessment and exergy analysis. J Clean Prod 2016;113:459–71. https://doi.org/10.1016/j.jclepro.2015.11.095.

[47] Patterson T, Esteves S, Dinsdale R, Guwy A, Maddy J. Life cycle assessment of biohydrogen and biomethane production and utilisation as a vehicle fuel. Bioresour Technol 2013;131:235–45. https://doi.org/10.1016/j.biortech.2012.12.109.

[48] Behrooznia L, Sharifi M, Hosseinzadeh-Bandbafha H. Comparative life cycle environmental impacts of two scenarios for managing an organic fraction of municipal solid waste in Rasht-Iran. J Clean Prod 2020;268. https://doi.org/10.1016/j.jclepro.2020.122217.

[49] Edwards J, Othman M, Crossin E, Burn S. Life cycle assessment to compare the environmental impact of seven contemporary food waste management systems. Bioresour Technol 2018;248:156–73. https://doi.org/10.1016/j.biortech.2017.06.070.

[50] Silva Lora EE, Escobar Palacio JC, Rocha MH, Grillo Renó ML, Venturini OJ, Almazán del Olmo O. Issues to consider, existing tools and constraints in biofuels sustainability assessments. Energy 2011;36:2097–110. https://doi.org/10.1016/j.energy.2010.06.012.

[51] Mayer F, Bhandari R, Gäth S. Critical review on life cycle assessment of conventional and innovative waste-to-energy technologies. Sci Total Environ 2019;672:708–21. https://doi.org/10.1016/j.scitotenv.2019.03.449.

[52] Camacho CI, Estévez S, Conde JJ, Feijoo G, Moreira MT. Dark fermentation as an environmentally sustainable WIN-WIN solution for bioenergy production. J Clean Prod 2022;374. https://doi.org/10.1016/j.jclepro.2022.134026.

[53] Wulf C, Kaltschmitt M. Life cycle assessment of biohydrogen production as a transportation fuel in Germany. 2013. https://doi.org/10.1016/j.biortech.2013.08.127.

[54] Djomo SN, Blumberga D. Comparative life cycle assessment of three biohydrogen pathways. Bioresour Technol 2011;102:2684–94. https://doi.org/10.1016/J.BIORTECH.2010.10.139.

[55] Manish S, Banerjee R. Comparison of biohydrogen production processes. Int J Hydrogen Energy 2008;33:279–86. https://doi.org/10.1016/j.ijhydene.2007.07.026.

[56] Reaño RL. Assessment of environmental impact and energy performance of rice husk utilization in various biohydrogen production pathways. Bioresour Technol 2020;299:122590. https://doi.org/10.1016/J.BIORTECH.2019.122590.