



Original Research

Large-scale commercial-grade volatile fatty acids production from sewage sludge and food waste: A holistic environmental assessment

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ABSTRACT

The valorization of sewage sludge and food waste to produce energy and fertilizers is a well-established strategy within the circular economy. Despite the success of numerous laboratory-scale experiments in converting waste into high-value products such as volatile fatty acids (VFAs), large-scale implementation remains limited due to various technical and environmental challenges. Here, we evaluate the environmental performance of a hypothetical large-scale VFAs biorefinery located in Galicia, Spain, which integrates fermentation and purification processes to obtain commercial-grade VFAs based on primary data from pilot plant operations. We identify potential environmental hotspots, assess the influence of different feedstocks, and perform sensitivity analyses on critical factors like transportation distances and pH control methods, using life cycle assessment. Our findings reveal that, on a per-product basis, food waste provides superior environmental performance compared to sewage sludge, which, conversely, performs better when assessed per mass of waste valorized. This suggests that higher process productivity from more suitable wastes leads to lower environmental impacts but must be balanced against increased energy and chemical consumption, as food waste processing requires more electricity for pretreatment and solid-liquid separation. Further analysis reveals that the main operational impacts are chemical-related, primarily due to the use of NaOH for pH adjustment. Additionally, facility location is critical, potentially accounting for up to 99% of operational impacts due to transportation. Overall, our analysis demonstrates that the proposed VFAs biorefinery has a carbon footprint comparable to other bio-based technologies. However, enhancements in VFAs purification processes are necessary to fully replace petrochemical production. These findings highlight the potential of waste valorization into VFAs as a sustainable alternative, emphasizing the importance of process optimization and strategic facility placement.

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1. Introduction

The average European Union citizen generated 5 t of waste in 2022, mostly mineral waste (i.e., demolition, mining, construction) (64%). When this type of waste is not considered, the production results in 1.8 t, with waste and water services accounting for 27.2%,

households for 24.2%, and manufacturing for 20.9%, representing the largest contributing activities [1]. In absolute terms, 519 kg per person (28.8%) is municipal solid waste, with a large amount of organic food waste (FW): 132 kg per person per year, with 55% from households and 19% from manufacturing [2]. Around 17% of municipal solid waste is valorized through composting and anaerobic digestion, but the percentage should be superior since 25.4% is organic waste [3]. Although not as relevant as for the waste production in households and manufacturing, wastewater management also generates organic wastes with representativeness for sewage sludge (SS) of 3.3% (around 16 kg dry matter per person per year) [2]. The management of SS has been identified as a major concern in wastewater management because of its potential for

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Abbreviations

AC	Acidification
BMP	Biomethane potential
BOD	Biological oxygen demand
CC	Climate change
CIP	Clean in place
CHP	Combined Heat and Power
COD	Chemical oxygen demand
FE	Freshwater eutrophication
FRS	Fossil resource scarcity
FW	Food waste
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LLE	Liquid–liquid extraction
ME	Marine eutrophication
MRS	Mineral resource scarcity
NF	Nanofiltration
OD	Ozone depletion
PHAs	Polyhydroxyalkanoates
RO	Reverse osmosis
SS	Sewage sludge
TS	Total solids
UF	Ultrafiltration
VFAs	Volatile fatty acids
VS	Volatile solids
THP	Thermal hydrolysis pretreatment
WC	Water consumption
WWTP	Wastewater treatment plant

adsorption of non-biodegradable pollutants such as metals, microplastics, antibiotics, and other emerging compounds [4]. These compounds can end up in agricultural soils since, because of their nitrogen and phosphorus content, the major application of the sludge in Europe is for agricultural purposes (around 47%), being valorized as fertilizer [2].

However, in the quest for climate neutrality and the reduction of co-dependence on counterpart production from fossil resources, the possibility of recovering/generating bio-products from urban organic wastes (specifically from SS and FW) should be investigated. Although biogas production to replace natural gas is an alternative, other products of higher added value can be obtained, such as acids, alcohols, antioxidants, enzymes, polymers, etc. [5]. In the field of organic acids, acetic acid is mainly produced by heterogeneous catalysis via the carbonylation of methanol or through fermentative routes [6,7]. Along with acetic acid, other volatile fatty acids (VFAs) can be produced during acetogenesis under anaerobic conditions: propionic and butyric acids. Although these two compounds have much lower commercial representativeness than acetic acid, they are relevant in producing propionates, butanoates, and esters for manufacturing food preservatives and flavorings [8]. In addition, VFAs production is also important in the plastics industry, as they are precursors of biopolymers [9]. Despite the possibility of generating VFAs from the bioconversion of organic matter, nowadays, those of high grade come from petrochemical derivatives processing and set the reference for market pricing [10]. The global acetic acid market reached a value of €8.6 billion in 2019, with projections of reaching €12 billion by 2025 and a market price of approximately €800 t⁻¹. The propionic acid market generated €1.2 billion in 2018 and is expected to reach €1.6 billion by 2026, with a market price of around €1300 t⁻¹. As for butyric acid, it is expected to reach a market size of about €170 million by 2026, and it holds the highest market price among VFAs at approximately €1800 t⁻¹ [11].

From a technological perspective, bio-based processes for VFAs production are expected to overcome the drawbacks associated with their petrochemical counterparts (carbonylation of methanol to acetic acid, hydrocarboxylation of ethylene to propionic acid, and

oxidation of butyraldehyde to butyric acid), such as high energy intensity, the use of non-renewable resources and the environmental impact of chemical waste discharges [12,13]. However, fermentative systems may have technical limitations such as yield, low process productivity, inhibition problems, slow bacterial growth, and low product concentration [14]. The lower purity of the product implies additional barriers: the higher energy and chemical consumption associated with distillation, evaporation, adsorption, filtration, or neutralization [15]. Besides this, bio-based technologies may threaten the social pillar of sustainability if the feedstocks used to produce the VFAs can also be used as food (i.e., maize) [16]. Therefore, these products must be produced from waste biomass to maintain the end-consumer market prices in the food supply chain [17]. Using residues for VFAs production provides a waste management alternative and is a feasible strategy for closing the material cycle within a circular economy approach [18]. In this regard, waste treatment and added-value product manufacturing should be considered functions of the newly designed factories.

Therefore, it should stand to reason that using an integrated facility offering valuable products while managing waste should have higher environmental protection, reduced resource consumption, and lower emissions. However, many conventional processes already in place have high efficiency, which has improved over years of operation and research. Therefore, optimizing processes with an environmental perspective should be performed at each level of technology maturity. At different scales, the environmental impacts for the production of VFAs have been analyzed mainly for three types of feedstocks: wastewater and sludges, bio-waste, and agricultural biomass (i.e., white birch, poplar biomass, wheat straw, sugar cane bagasse, corn stover, sugar beet molasses and seaweed) [19–23]. Within the wastewater sector, five publications can be highlighted (two for valorization of wastewater and three for SS). The environmental performance of VFA production from wastewater was only studied at a laboratory scale by fermentation [24,25]. Using biological processes, the environmental burdens of VFAs production from SS were investigated at different scales to produce polyhydroxyalkanoates (PHAs). The direct commercialization of VFAs after purification was not foreseen [26–28]. Regarding FW, three other studies have been reported: those of Pinto et al. [29], Soleymani-Angili et al. [30] and Elginöz et al. [31]. Of the three, only the first one considered the purification of VFAs through pervaporation and electrodialysis. In this regard, there seems to be a gap in the environmental analysis of large installations for VFAs manufacturing and in comparing performance for the same process and different types of waste. More specifically, the operation of the same facility using SS or FW was not analyzed, considering its possible environmental impacts. On the other hand, the environmental analysis has focused on identifying technological or process critical impacts without extending the study beyond the facility gates. The impact of technologies such as biomass fractionation and dewatering has been tested, but most studies used fermentation as the core technology. Distillation was the preferred option for VFAs purification. Despite their popularity, the environmental performance of these technologies has been studied independently for non-agricultural biomass. Beyond a technological approach and for large-scale facilities, their impacts can also be related to their location, which implies that specific solutions should be found for aspects like transportation or water scarcity of regions, among others.

Based on this context, a biorefinery using SS and FW as feedstock is analyzed in this study. Primary data were collected from a pilot plant facility in Galicia (northwest Spain) for producing commercial-grade chemicals (acetic, propionic, and butyric acids) through fermentation. These data were used to scale up the process

and to compile the inventory of energy, chemicals, and emissions for the full-scale facility. The integral process was evaluated by performing a life cycle assessment, which includes an analysis of environmental hotspots, a benchmarking of the operation of the facility for two wastes (with two functional units to consider a product and waste management approach), a sensitivity analysis for critical impacts (transportation and chemicals for pH control in the fermentation) and a comparison of the carbon footprint results with others reported in the literature.

2. Materials, methods, and methodology

2.1. Data collection: description of the pilot-scale technology

Composition of the feedstocks and process data such as VFA yields, selectivity, and chemical consumption were collected from a fermentation pilot plant, including downstream processes for VFAs purification: membrane technology and liquid–liquid extraction (LLE) [32]. The gray area of Fig. 1 shows the boundaries of the pilot-scale facility. The remaining equipment shown in the figure is described in Section 2.2 and included in the scale-up. The information provided below for this section has been intentionally described to highlight the origin and methods for procuring the primary data.

Hydrolyzed SS or FW were characterized and used as input biomass to be valorized the pilot facility. The hydrolyzed SS used was collected in a wastewater treatment plant (WWTP) in north-west Spain. The WWTP operated with a full-scale high-pressure

thermal hydrolysis pretreatment (THP), which is fed with a mixture of primary sludge (70% chemical oxygen demand [COD]) and biological sludge (30% COD). Its characterization is similar to that reported by Liu et al. [33] in terms of total solids (TS) and volatile solids (VS) being, in this case, the VS/TS ratio higher than the one reported (80.1% versus 57.6%, respectively). Apart from this, the considered substrate has 15.3% of its total COD in soluble form, 9% of total solids, and an acidic pH of 6.3.

Regarding FW, it was collected from expired products and left-over food from a supermarket. The composition was 50% fruit and vegetables, 25% bread, pastries, and pasta, and 25% meat and fish (by weight). This composition matches well with those reported by Hansen et al. [34] and Khatami et al. [35], being representative of that generated in Southern Europe. The FW has a humidity of 80% and a pH of 4.9. All these wastes were shredded, and water was added to achieve the desired dilution. For the physicochemical characterization of the waste (shown in Table S10 of Supplementary Materials), TS and VS were determined as specified in Ref. [36]. Measurements of total COD and soluble COD were performed using the Hach LCK cuvette test system: total COD was measured using the raw sample, while for soluble COD, the sample was centrifuged at 6000 rpm for 10 min and then filtered through Whatman GF/C filters with a 0.45 μm pore size. More information about the physicochemical composition of the substrates (SS or FW) was detailed in Castro Fernández et al. [32,37], and more data have also been summarized in Table S10 (Supplementary Material).

Once the properties of the feedstock had been identified, both SS and FW were fed to the fermentation reactor. The operation yielded

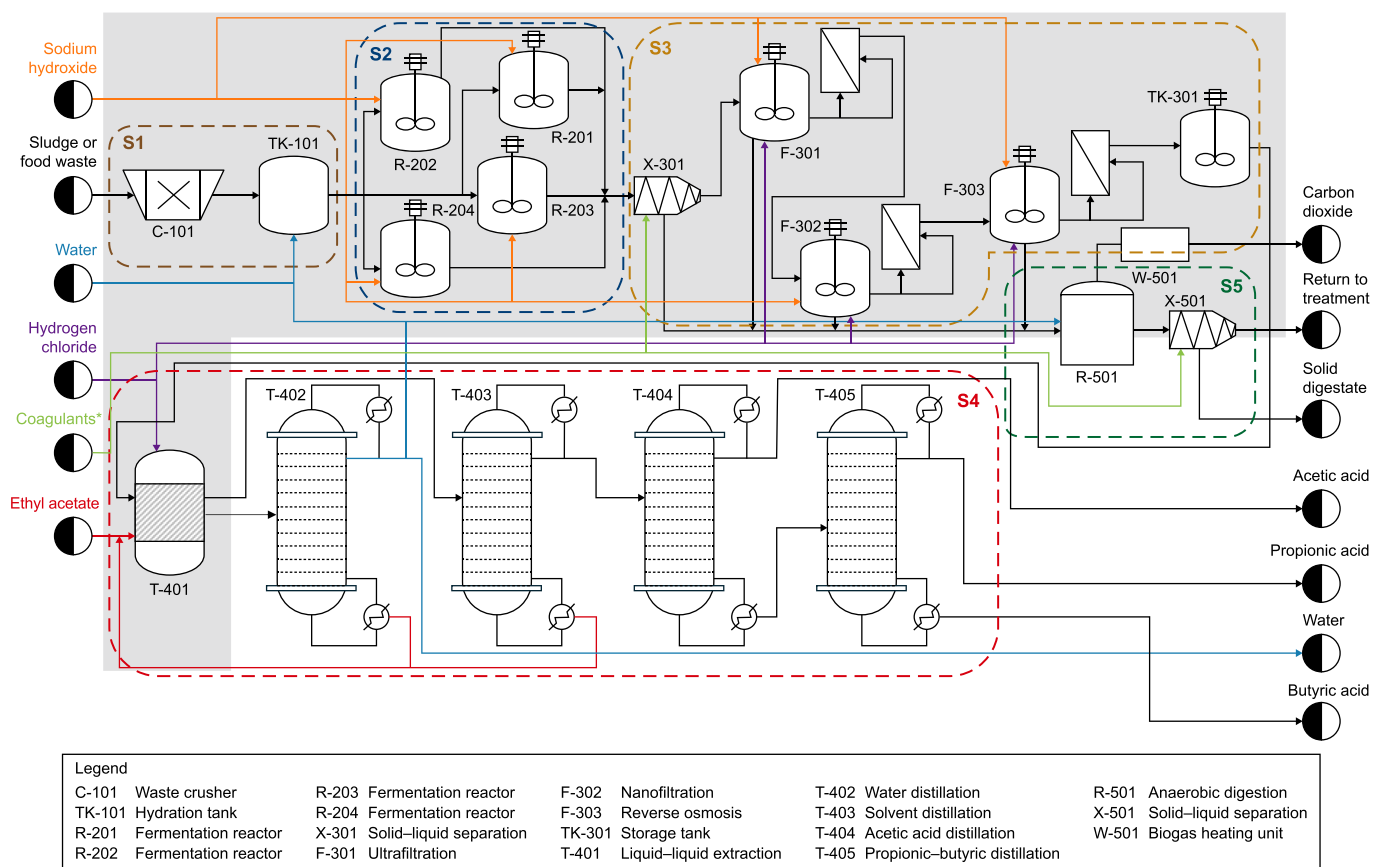


Fig. 1. Plug flow diagram of the sewage sludge or food waste biorefinery. The gray shading indicates the boundaries from which the pilot-scale primary data were collected. The color of the arrows is related to the chemical fed to each equipment. S1: Pretreatment and water addition; S2: Fermentation; S3: Solid-liquid separation and VFAs pre-concentration; S4: VFAs purification; S5: Solid fraction digestion.

VFA yields of 0.12 g COD-VFAs per g COD for SS and 0.37 g COD-VFAs per g COD for FW at pH 8.5 and 7.0, respectively. Regarding VFAs production selectivity, the spectrum differed markedly between SS and FW, being 80% acetic acid, 10% propionic acid, and 10% butyric acid for SS in mass basis and 40% acetic, 20% propionic, and 40% butyric for FW [32,37].

The downstream processes for purification of the VFAs obtained in the fermentation were also tested on a pilot scale. The membrane train (composed of ultra, nano, and reverse osmosis) fed by the liquid fraction of fermentation achieved a final concentration of 50 g VFAs L⁻¹. Subsequently, this stream was subjected to LLE using ethyl acetate as a solvent; total recovery of VFAs was accomplished by applying a solvent/feeding ratio of 0.75 kg kg⁻¹ (optimum when a balance is sought between extraction capacity and related costs). The separation of the VFAs from the solvent and the acids from each other was simulated and was described in more detail in Section S3.3 of Supplementary Materials.

2.2. Scale-up and process design

All the experimental information from the pilot plant has served as the base for developing a tool in a Microsoft Excel® spreadsheet, which integrates all the mass and energy balances of the VFAs biorefineries. Thus, two scenarios have been chosen: the first would be the operation of a VFA plant treating all the SS generated in the Autonomous Community of Galicia (northwest of Spain), and the second would be a plant treating all the FW from the same region. The process is the same for both substrates; the only thing that would be modified is the pretreatment stage (subsection S1 in Fig. 1), which should include a shredding stage in the second scenario. From now on, the scenarios will be named according to the substrate fed to the system.

Around 68,000 t dry matter of SS year⁻¹ are produced in Galicia - calculated considered a generation of 70 g of TS per capita per day of SS [38] and a population of 2.7 million inhabitants [39]. In this region, SS has been treated with external waste managers focusing on agricultural applications after disinfection, composting, and soil amendment. Therefore, the design of a treatment facility that goes beyond the agricultural use of sludge may be an answer when applying the sludge to soils is no longer an option. The average dryness of WWTP's SS to be treated in Galicia for an external management company is around 18% (although it varies between 7 and 32% depending on the technologies implemented for moisture reduction). Regarding FW, around 22,174 t DM year⁻¹ would be available in Galicia, considering a separate collection rate of 25%. It should be noted that the maximum achievable amount of FW that could be collected in urban environments was around 85%, depending on the year, but Galicia does not have a well-established FW collection strategy, with a relevant fraction being improperly deposited in the wrong container. Information on the annual treatment capacity and VFAs production can be found in Table S12 (Supplementary Material). Further data on life cycle inventories are also shown in Section 2.3.2. It should also be considered that the composition of the SS and FW for the pilot and full-scale facilities were assumed to be the same. The operation of the scaled-up facility should be tested in future research for the regional composition of SS since not all the Galician WWTPs have technologies such as THP to pretreat the sludge.

The biorefinery was divided into five sub-sections: pretreatment and water addition (S1), fermentation (S2), solid-liquid separation and VFAs pre-concentration (S3), VFAs purification (S4), and solid fraction digestion (S5) (Fig. 1). It is assumed that the SS from the WWTPs in Galicia and the FW are collected and transported by truck to the facility. After reception, water was added to SS or FW to reach a solids concentration suitable for fermentation (section S2).

The dilution of the substrates to 7% TS was done with a water stream from one of the VFAs distillation columns (T-402), which can be considered a circularity strategy during the facility's design. After pre-treatment in section S1, the waste stream is fed to the fermentation reactors (R-201 to R-204 in Fig. 1) at mesophilic temperature (37 °C). Since pH decreases during the acidification stage, NaOH was continuously added to the reaction to ensure stable operation. The reactor is assumed to be perfectly sealed, and no gaseous emissions were foreseen. This is because the reactor was specifically operated to convert organic matter directly into VFAs. The fermented solid effluent was separated into solid and liquid fractions. A coagulant and a flocculant (Floquat FL3249 and Flopam EM840CT) were added, followed by centrifugation. The cake was valorized in the S5 section, while the liquid fraction was subsequently fed to a filtration train to remove impurities such as proteins, sugars, and so on.

After passing through the ultrafiltration and nanofiltration membranes, the purified VFAs-rich stream was concentrated by reverse osmosis. The cleaning-in-place (CIP) method used NaOH, HCl, and water for membrane cleaning. After membrane treatment, the preconcentrated VFAs solution was subjected to LLE with ethyl acetate and distillation processes to recover a mixture of high-purity VFAs and the solvent (T-403). This mixture is fed to two additional distillation processes (T-404 and T-405) in series, and thus, commercial-grade acetic, propionic, and butyric acids are obtained. Unit T-402 is needed to recover the solvent lost in the LLE's raffinate.

As for the solid fraction obtained after centrifugation in section S3, it is fed to a mesophilic anaerobic digester together with the rejection from the ultrafiltration (F-301) and nanofiltration (F-302) membranes and the reverse osmosis permeate (F-303) to produce biogas. This is first sent to a boiler to cover the thermal needs of the fermentation and distillation processes. The surplus biogas is sent to a cogeneration engine to produce the electricity needed for the whole process. After this mesophilic digestion, an additional solid-liquid separation with its associated polyelectrolyte consumption would be necessary to obtain the final solid fraction to be managed externally.

2.3. Life cycle assessment

Life cycle assessment (LCA) is the methodology used to unveil the environmental profile of SS and FW valorization to produce commercial-grade acetic, propionic, and butyric acids. The analysis was performed considering the guidelines detailed in ISO 14,040 and 14,044 with a product-based and process-based approach considering [40,41]: (1) a comparative assessment of the facility under operation feeding two feedstocks with different characterization, (2) a comparison of the footprint of bio-based VFAs production, ensuring consistency of results between functional units, (3) detection of process hotspots, (4) proposal of actions for future improvement of the critical impacts (sensitivity analysis for transportation and sodium hydroxide as pH control chemical), and (5) background of CO₂ emissions for future research on the production of VFAs. For this reason, a systematic literature review was conducted to investigate LCA assumptions and procedures followed. Methodological aspects such as method selection, functional unit, and impact categories were supported by the literature review results. Tables S2–S9 (included in Supplementary Materials) depict the main findings reported. On the other hand, the results of this research were compared with those of other bioprocesses, leading to the manufacture of VFAs and other traditional technologies specialized in producing acetic, propionic, and butyric acids. More details about how this benchmarking was done are described in Section 2.3.3.

2.3.1. Definition of the system boundaries and functional unit

This study provides a cradle-to-gate analysis with system boundaries subdivided into foreground and background processes. As in any other LCA, the foreground system accounts for direct emissions produced during facility operation and/or equipment construction. Both the SS and FW scenarios only emitted CO₂, which comes from the valorization of the biogas into heat and electricity. Although SS and FW can be contemplated as bio-based materials, the emissions have not been considered biogenic. This aligns with the methodological guidelines provided by the [42]. For example, SS is a waste stream from urban WWTPs. These facilities treat domestic wastewater and organic matter associated with industrial activities that use fossil-based chemicals. The technical limits have been limited to the operational phase. This is because the primary data come from the operation of a pilot-scale fermentation stage, not from its construction. The geographical limits of the system have been restricted to Europe. However, exceptions have been made for NaOH and ethyl acetate, as the Ecoinvent V3.8 database does not yet have characterization factors for these processes at the European level [43]. Therefore, the impact of these two processes on a global scale was assumed to be equivalent to that of a similar process installation located in Europe. The transportation of chemicals was assumed to be 141.31 km, which was the average distance for freight transportation within Europe in 2022 [44]. The impacts of the SS or FW transportation reference scenarios were assumed similarly to those mentioned for chemicals. A sensitivity analysis was described in Section 2.3.4 to reduce the environmental burdens associated with transportation. Apart from this, no other impacts were assigned to processing the waste. If cradle impacts are considered, SS and FW should have the respective impacts on the facilities from which they were collected. In the case of SS, the analysis should include tap water collection, use, and wastewater treatment, which is beyond the scope of this research work. Given that the system is multifunctional, the LCA could have both a process and a product approach, and two functional units are defined: 1 t of valorized waste (SS or FW, depending on the scenario) and 1 t of VFAs produced.

2.3.2. Life-cycle inventory

The life cycle inventory (LCI) has been collected using an attributional and bottom-up approach (for the foreground process). As shown in Table 1 and 2, the data were classified into three groups: inputs from the Technosphere for chemicals and energy consumed by the facility, outputs to the Technosphere for manufactured products, and waste streams and outputs to the Ecosphere (nature) for direct emissions. In each of the tables, information is given for each functional unit and the two scenarios compared, respectively. Both primary and secondary data were used to create the LCI inventories due to the scale-up for the foreground process and the use of background data from the Ecoinvent V3.8 database.

2.3.3. Life cycle impact assessment: selection of method and categories

The translation of the LCI into environmental impacts has been conducted with the support of the SimaPro® software version 9.6.0.1. For this purpose, the program uses the characterization, normalization, or weighting factors from life cycle impact assessment (LCIA) methods. A MidPoint approach was followed to determine the environmental impact categories, and among the possible LCIA methods found in SimaPro (CML, Cumulative Energy Demand, Ecological Scarcity, Environmental Footprint, IMPACT World, ReCiPe, TRACI, and USEtox), Environmental footprint V3.0 was selected. Multiple reasons were behind its selection: the method is not outdated, it can result in a multi-criteria assessment with more than one category calculated, the characterization

Table 1

Inventory of the VFAs production from sludge or food waste (functional unit of 1 t waste).

Inputs from the Technosphere	SS scenario	FW scenario
Generic		
Electricity for pumping (kWh)	1.47	1.84
Transportation of substrate (t km)	141.31	141.31
S1: Pretreatment and hydration		
Electricity C-101 (kWh)	0.00	20.00
Water TK-101 (m ³)	1.25	1.72
S2: Fermentation		
Sodium hydroxide R-201 to R-204 (kg)	15.43	13.33
Heating R-201 to R-204 (kWh)	13.66	0.00
Electricity for stirring R-201 to R-204 (kWh)	1.85	1.20
S3: Solid-liquid separation and VFAs preconcentration		
Coagulant X-301 (kg)	0.06	0.17
Flocculant X-301 (kg)	0.04	0.13
Electricity X-301 (kWh)	5.14	6.99
Water for cleaning F-301 (m ³)	0.30	0.42
Sodium hydroxide F-301 (kg)	1.62	2.23
Hydrogen chloride for cleaning F-301 (kg)	1.40×10^{-3}	1.93×10^{-3}
Electricity F-301 (kWh)	4.15×10^{-3}	5.70×10^{-3}
Water for cleaning F-302 (m ³)	0.05	0.07
Sodium hydroxide F-302 (kg)	1.54	2.12
Hydrogen chloride for cleaning F-302 (kg)	1.33×10^{-3}	1.83×10^{-3}
Electricity F-302 (kWh)	5.91×10^{-3}	5.42×10^{-3}
Water for cleaning F-303 (m ³)	4.59×10^{-2}	6.30×10^{-2}
Sodium hydroxide F-303 (kg)	0.69	0.95
Hydrogen chloride for cleaning F-303 (kg)	0.85	1.17
Electricity F-303 (kWh)	7.49×10^{-3}	7.72×10^{-3}
S4: VFAs purification		
Hydrogen chloride before T-401 (kg)	2.29	3.14
Ethyl acetate T-401 (kg)	0.37	0.51
Heating T-402 (kWh)	2.53×10^{-2}	0.00
Heating T-403 (kWh)	9.71×10^{-3}	0.00
Heating T-404 (kWh)	1.35×10^{-3}	0.00
Heating T-405 (kWh)	3.24×10^{-4}	0.00
Electricity T-401 to T-405 (kWh)	1.10	0.11
S5: Solid fraction digestion		
Water for hydration before R-501 (m ³)	0.76	0.63
Polyelectrolyte X-501 (kg)	1.37	2.75
Heating R-501 (kWh)	7.77	0.00
Electricity for stirring R-501 (kWh)	2.10	1.58
Outputs to the Technosphere	SS scenario	FW scenario
Products		
Acetic acid (kg)	13.01	22.61
Butyric acid (kg)	1.67	9.56
Propionic acid (kg)	0.42	9.74
Residues		
Solid cake from R-501 digestate (kg)	0.43	0.31
Wastewater returns (m ³)	1.04	0.79
Membrane cleaning water (m ³)	0.47	0.65
Outputs to the Ecosphere		
Carbon dioxide from biogas-burning units (kg)	86.32	177.65

factors are provided at the European level, it is not a commonly used method (as shown in Table S9 in Supplementary Materials) but recommended by the European Commission (as indicated in Commission Recommendation (EU) 2021/2279).

The impact categories were selected among those of the method: climate change (CC), ozone depletion (OD), acidification (AC), freshwater eutrophication (FE), marine eutrophication (ME), water consumption (WC), fossil resource scarcity (FRS), and mineral resource scarcity (MRS). Tables S6–S8 (Supplementary Materials) provide an overview of the literature's most used impact categories. Although the categories were selected based on the study's objectives and the feasibility of comparison with other studies, information was also depicted in Fig. S1 (Supplementary Material) to show the relevancy of the impact categories after applying normalization factors from the EF3.0 method. One common characteristic for all the LCA publications (on fermentation and other technologies for VFA production) considered for the critical review is reporting outcomes related to climate change or global warming

(93% of representativeness among studies). The anticipation of changes related to global warming can be done by measuring gases released and trapped into the atmosphere, in other words, by estimating the carbon footprint or the emission of equivalent CO₂ emissions. Therefore, different research studies analyzing bioprocesses and other traditional technologies leading to the manufacture of VFAs can be compared through this common impact category of the LCA. For the above reasons, the analysis of the VFAs production process from SS and FW described within this research has been done with a multicriteria analysis of several categories, but the comparison and discussion of results with other studies has been done only considering the climate change category (or carbon footprint).

2.3.4. Sensitivity analysis: transportation and chemical use

Sensitivity analyses were carried out for the two most critical aspects of VFAs production. For transportation, although an average European road freight distance of 141.31 km was considered [44], other options associated with the relative location of WWTPs in the reference area were evaluated so that maximum and minimum distances between WWTPs were estimated, as well as an optimal distance. In the case of SS, 97 WWTPs were mapped in June 2024 using Google Earth and Google Maps. The distance transported by road to the other 96 identified facilities was recorded for each WWTP. The Supplementary Materials provide an Excel database of estimated distances and fastest transportation routes according to Google Maps. The longest distance between the two facilities is 330 km, which corresponds to the route between the WWTPs of A Guarda and Ribadeo. The shortest distance is 3.9 km (Betanzos to/from Miodelo). These two distances created the “maximum” and “minimum” distance scenarios. Apart from these and the baseline, two further alternatives were compared. One assumed that a cargo truck transported the SS in closed containers. The last scenario results from optimizing the distance transportation according to the SS produced at each WWTP. The idea is to select, among the existing facilities, the minimum transportation of the waste collected from the others. The optimal average distance To transport the SS is 77.4 km. For the treatment of all SS in Galicia, the best location belongs to Moraña, followed by Valga (80.3 km), Pontevea (81 km), and Padrón (81.3 km). In addition, there are 11 other WWTPs with transportation distances between 80 and 90 km. More information on the distribution of the road distances of the SS transportation facility can be found in Fig. S3 (Supplementary Material). In addition, Fig. S4 (Supplementary Materials) shows the location of each WWTP included in the investigation. Although the facility was designed for the whole region of Galicia, the optimal distances per province were also estimated. For Pontevedra, the optimum distance of excess is 33 km, with the best location for the biorefinery being in the town of Vilaboa. For Ourense, it is 8.8 km, corresponding to the Ourense WWTP. In the case of Lugo, it is 22 km, and the location should be the facility in the city of Lugo. Finally, the region of A Coruña needs to locate the biorefinery at the Bens WWTP, with an optimal average sludge transportation distance of 44 km.

The transportation distance estimation strategy could not be applied when dealing with FW. This is because the FW treatment infrastructures for the Galicia region are under construction and, therefore, could not be located on Google Maps to determine road transportation distances. However, the facilities have been positioned to have transportation distances of less than 50 km (Galician Order of November 30, 2021, DOG number 238). This is the value assumed in this research to compare changes in the environmental profile based on FW transportation.

A direct reduction can lead to an inherent decrease in impacts and costs for chemicals, provided that VFAs and biogas production

are not changed. Future studies should be conducted on the existing pilot scale to verify this issue. What is less straightforward is determining whether the use of other chemicals decreases the impact, as each chemical has its associated manufacturing process. Therefore, the sensitivity analysis proposed for this section tries to give hypothetical results if NaOH was replaced by KOH or Mg(OH)₂. The same OH input concentration was assumed, and fermentation performance was similar in the presence of potassium or magnesium ions.

3. Results

3.1. Environmental analysis of inventory

Tables 1 and 2 show the relevant inputs and outputs of the two compared scenarios with two different functional units. For a clearer description, the results obtained will be provided, considering the performance of the processes in terms of energy and chemicals. Regarding energy, the SS scenario reports a 5.61% higher demand than the FW scenario per t of waste valorized. The same picture is consistent when the functional unit is changed to 1 t VFAs produced. The difference between the two scenarios, however, is higher for this case (62.7%), which can be attributed to the higher VFAs production of the FW scenario (15.1 kg VFAs per t SS versus 41.9 kg VFAs per t FW) and implies that the FW scenario is more energy efficient than the SS one. The distribution of energy within the process is different. The SS profile is mainly characterized by energy use in the biological processes (49% for S2 or fermentation and 31% for S5 or digestion of solid fractions). However, FW allocates energy to pretreatment (67%) due to the need for shredding and solid-liquid separation (23%). Although both processes are almost identical in terms of infrastructure, their dissimilarity in operation is related to the composition of the waste streams. Furthermore, the solid cake obtained after fermentation has a much higher potential for methane production than the one obtained from SS (in particular, 447 versus 184 L(N) CH₄ per kg VS as evidenced in the BMP (biomethane potential) test, Fig. S2). Therefore, on-site valorization of biogas as heat has proven to be a good strategy to decrease the external demand and thus reduce the relative heating consumption for the FW scenario. The heating decrease in the FW scenario offsets the electricity used in grinding and leads to an absolute win-win profile.

Regarding chemicals, the use of NaOH for pH control in the fermenter and membrane cleaning activities account for 70–80% by mass (depending on the scenario). It should be noted that water has been left out of this accounting, and only consumables such as NaOH, HCl, ethyl acetate, coagulant, flocculant, and polyelectrolyte were considered. The overall mass difference between the two scenarios is about 8.4%, which is low considering that the FW almost doubles the total solids content of SS. The FW scenario reports a higher demand for chemicals (between 1.36 and 2.08) except for NaOH (which is 3.38% lower). This is because the optimum yields for the SS and FW scenarios were achieved at pH 8.5 and 7, respectively. It is worth mentioning that the primary data collected at the pilot scale corresponds to the continuous process monitoring. In this sense, the NaOH results reveal changes in terms of initial pH modification and monitoring during operation (around 2–3 kg NaOH m⁻³ fed to the reactor). Changing the functional unit to 1 t VFAs produced reports a much larger influence on NaOH consumption. However, these results are biased by the higher VFAs production capacity of the FW scenario.

3.2. Comparison between scenarios

The problem with a stand-alone LCI analysis is that it does not

Table 2
Inventory of the VFA production from sludge or food waste (functional unit of 1 t VFAs).

Inputs from the Technosphere	SS scenario	FW scenario
Generic		
Electricity for pumping (kWh)	89.44	44.20
Transportation of substrate (t km)	8585.90	3389.67
S1: Pretreatment and hydration		
Electricity C-101 (kWh)	0.00	479.76
Water TK-101 (m ³)	76.20	41.34
S2: Fermentation		
Sodium hydroxide R-201 to R-204 (kg)	937.43	319.84
Heating R-201 to R-204 (kWh)	830.11	0.00
Electricity for stirring R-201 to R-204 (kWh)	112.49	28.79
S3: Solid-liquid separation and VFAs preconcentration		
Coagulant X-301 (kg)	3.91	4.00
Flocculant X-301 (kg)	2.34	3.20
Electricity X-301 (kWh)	312.05	167.63
Water for cleaning F-301 (m ³)	18.53	10.05
Sodium hydroxide F-301 (kg)	98.68	53.54
Hydrogen chloride for cleaning F-301 (kg)	0.09	0.05
Electricity F-301 (kWh)	0.25	0.14
Water for cleaning F-302 (m ³)	2.93	1.59
Sodium hydroxide F-302 (kg)	93.74	50.86
Hydrogen chloride for cleaning F-302 (kg)	8.09×10^{-2}	4.39×10^{-2}
Electricity F-302 (kWh)	0.36	0.13
Water for cleaning F-303 (m ³)	2.79	1.51
Sodium hydroxide F-303 (kg)	41.81	22.69
Hydrogen chloride for cleaning F-303 (kg)	51.57	27.98
Electricity F-303 (kWh)	0.45	0.19
S4: VFAs purification		
Hydrogen chloride before T-401 (kg)	138.86	75.34
Ethyl acetate T-401 (kg)	22.67	12.18
Heating T-402 (kWh)	1.53	0.00
Heating T-403 (kWh)	0.59	0.00
Heating T-404 (kWh)	8.18×10^{-2}	0.00
Heating T-405 (kWh)	1.97×10^{-2}	0.00
Electricity T-401 to T-405 (kWh)	66.82	2.56
S5: Solid fraction digestion		
Water for hydration before R-501 (m ³)	46.29	15.00
Polyelectrolyte X-501 (kg)	82.99	65.95
Heating R-501 (kWh)	471.84	0.00
Electricity for stirring R-501 (kWh)	127.88	37.99
Outputs to the Technosphere	SS scenario	FW scenario
Products		
Acetic acid (kg)	790.73	542.36
Butyric acid (kg)	101.52	229.28
Propionic acid (kg)	25.64	233.70
Residues		
Solid cake from R-501 digestate (kg)	25.91	7.54
Wastewater returns (m ³)	62.90	18.84
Membrane cleaning water (m ³)	28.66	15.55
Outputs to the Ecosphere		
Carbon dioxide from biogas-burning units (kg)	5244.54	4261.40

consider the indirect impacts of producing different types of energy and chemicals. Therefore, the most polluting scenario may not necessarily be the one that consumes the most energy and/or chemicals. Therefore, the scenarios were also compared after the LCI data had been characterized at the LCIA stage. Although Section 3.1 shows the potential of the FW scenario in terms of energy and NaOH consumption, the results of the LCA show a controversy about which scenarios should be designated as the most environmentally friendly. The analysis of the results for 1 t of waste valorized (Fig. 2a) indicates that the processing of SS is the better option. With a change of the functional unit to contemplate the function of manufactured products, the FW scenario is by far the most environmentally friendly alternative (ranging from 25% for OD to 60% for MS), as indicated in Fig. 2b. This is because of the differences in the composition of the two wastes. As indicated in Section 3.1, the same weight of FW as SS (1 t) gives a much higher VFA yield. This results in higher production of acetic, propionic, and butyric acids and biogas. Since energy consumption and chemicals

have not increased dramatically (as indicated in absolute terms in Tables 1 and 2), this translates into a lower environmental impact per product unit.

3.3. Hotspot study of SS scenario

Seven items can be identified in Fig. 2 to clarify which section of the facility, emissions, or generic aspects (pumping and feedstock transportation) can be highlighted as critical, thus pointing them out for future facility enhancement. “Generic” seems to be the profile’s hotspot since it concerns half of the categories (around 57% for CC, 85% for AC, 92% for ME, and 79% for FRS). Transportation represents more than 99% of the previously mentioned categories’ scores. The second position stands out in the S2 section, where the fermentation occurs, and FE and MRS are the most affected. Sections S1 and S5 are also important for WC and OD, respectively. Concerning S2, NaOH has an impact between 82% (FRS) and 99% (WC). Therefore, the facility section is defined by chemical demand,

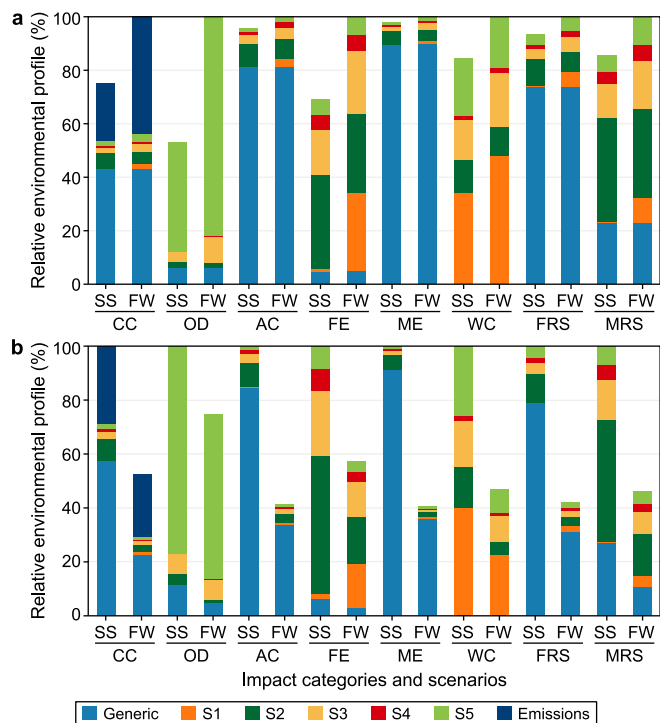


Fig. 2. Comparative and contribution relative environmental profile per facility section of the sewage sludge (SS) and food waste (FW) scenarios for 1 t of valorized waste (a) and 1 t of VFAs produced (b). CC: Climate change; OD: Ozone depletion; AC: Acidification; FE: Freshwater eutrophication; ME: Marine eutrophication; WC: Water consumption; FRS: Fossil resource scarcity; MRS: Mineral resource scarcity. S1: Pretreatment and hydration; S2: Fermentation; S3: Solid–liquid separation and VFAs preconcentration; S4: Volatile fatty acid purification; S5: Solid fraction digestion.

not energy. This outcome differs partially from the results achieved by Elginoz et al. [24], whose main contributing components are the heat to increase the reactor’s temperature and the NaOH demand for pH control. In this regard, it is demonstrated the relevancy of the energetic optimization of the system (with the valorization of the biogas from the solid cake obtained) and, thus, the heating up of fermenters and digesters or the stirring is no longer an environmental concern. Because there is no need for grinding, S1 has been only characterized by water consumption for hydration. In S5, the consumption of polyelectrolyte (99.9%) is the reason behind the score of OD.

Sewage sludge transportation to the facility is a key factor in ensuring a sustainable treatment since it could represent an impact up to 12 times bigger (i.e., ME) than the facility’s operation. Other important figures can be quoted for CC (2.3 times higher), AC (6.4 times), and FRS (4.6 times). Therefore, the selection of the location of the facility is something worth discussing during its construction. As this would also determine the facility’s daily operation, it has already been proposed as a sensitivity analysis in Section 2.3.4. Since the facility operator cannot implement changes once the location has been selected, the environmental profile of the installation should also be described. By completely eliminating substrate transportation, the relative contribution of the categories remains the same for WC and OD. All other categories would have S2 as the worrisome area of the facility. The same reasoning as mentioned above applies to NaOH consumption.

In line with what was mentioned, the SS transportation from its respective WWTP to the biorefinery leads the environmental profile in four of the eight categories under study (Fig. 3). The major impact of the other four (OD, FE, WC, and MRS) comes from the

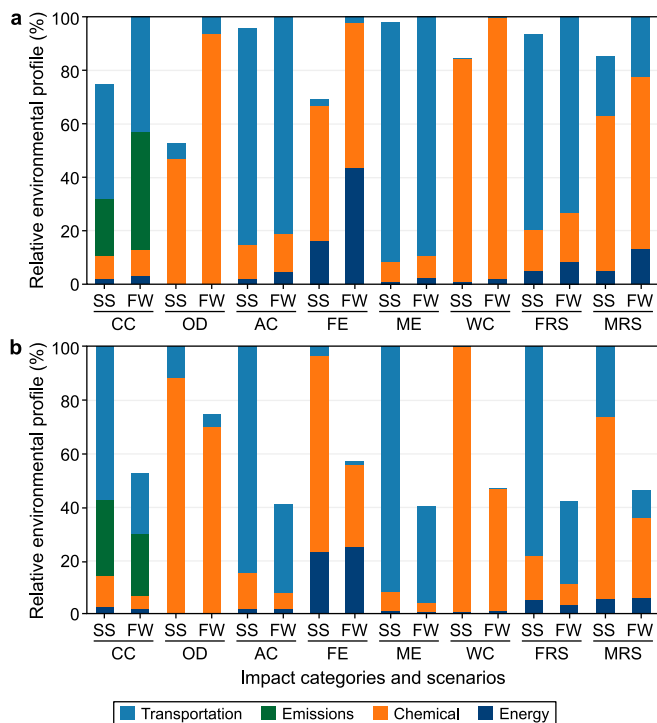


Fig. 3. Comparative and contribution relative environmental profile classified as energy, chemical, transportation, and emissions of the sewage sludge (SS) and food waste (FW) scenarios for 1 t of valorized waste (a) and 1 t of VFAs produced (b). CC: Climate change; OD: Ozone depletion; AC: Acidification; FE: Freshwater eutrophication; ME: Marine eutrophication; WC: Water consumption; FRS: Fossil resource scarcity; MRS: Mineral resource scarcity.

consumption of chemicals. Direct emissions, such as CO₂ from the valorization of biogas, have negligible impact in all categories except for CC (28.5%). Compared to transportation and chemicals, the contribution of energy is low (around 0.2–5.8% for OD and MRS) but higher for FE (23.4%). Within energy, electricity demand is the main concern in all categories except OD, where heating represents 69.3%. Solid–liquid separation is the facility’s activity with the biggest impact on electricity demand due to its remarkable consumption (20 kWh per t dry matter) [45]. These results differ from those obtained in the inventory analysis of Section 3.1, where energy in the biological processes was the main area of interest. This is because the environmental impacts of producing 1 kWh of European electricity are higher than producing the same amount of industrial heat. That is, 0.37 kg CO₂ per kWh of electricity is generated compared to 0.18 kg CO₂ per kWh for heat.

Therefore, the profile of SS is mainly characterized using energy in the biological processes (49% for S2 or fermentation and 31% for S5 or solid fraction digestion).

3.4. Hotspot study of FW scenario

Since the SS and FW scenarios share the same facility infrastructure, with the minor dissimilarities already highlighted in Section 3.3, the environmental outcomes of the FW scenario will be like those already provided for SS. Therefore, this section aims to indicate achievements different from those described in Section 3.3. When performing the study per facility section (as shown in Fig. 2), ranking the more relevant items inside each category remains the same. The only deviation can be found for CC since the share of the “generic” item in scenario FW decreased from 57% to 43%. Instead, the direct emission of CO₂ from the combustion and

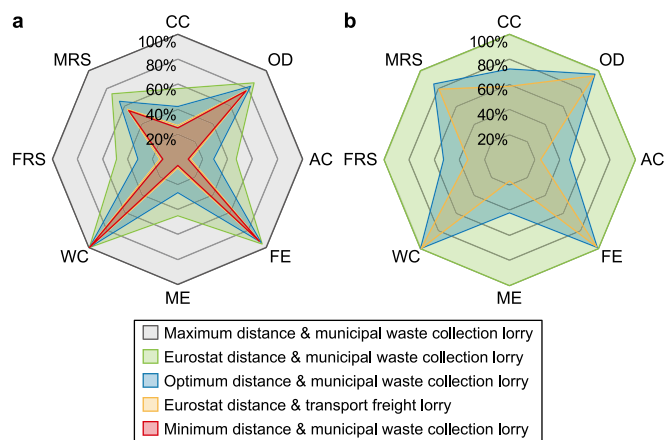


Fig. 4. Sensitivity analysis for the transportation of sewage sludge or food waste to the facility. **a**, 1 t of valorized waste and sewage sludge scenario; **b**, 1 t of valorized waste and food waste scenario. CC: Climate change; OD: Ozone depletion; AC: Acidification; FE: Freshwater eutrophication; ME: Marine eutrophication; WC: Water consumption; FRS: Fossil resource scarcity; MRS: Mineral resource scarcity.

valorization of the biogas from S5 became the dominant impact (this was caused by the larger biogas production). The use of biogas compensates for the heating in the fermenter (92%, as shown in the LCI) and anaerobic digestion reactors (83%) but not in terms of direct emissions (it is around 2 times higher). Apart from the emissions in CC, the results of Fig. 3 indicate a considerable reduction in the relevance of chemicals in FE (from 73% to 54%). This has been caused by a reduction in the consumption of NaOH in the process (as described in Section 3.1 for the LCI analysis).

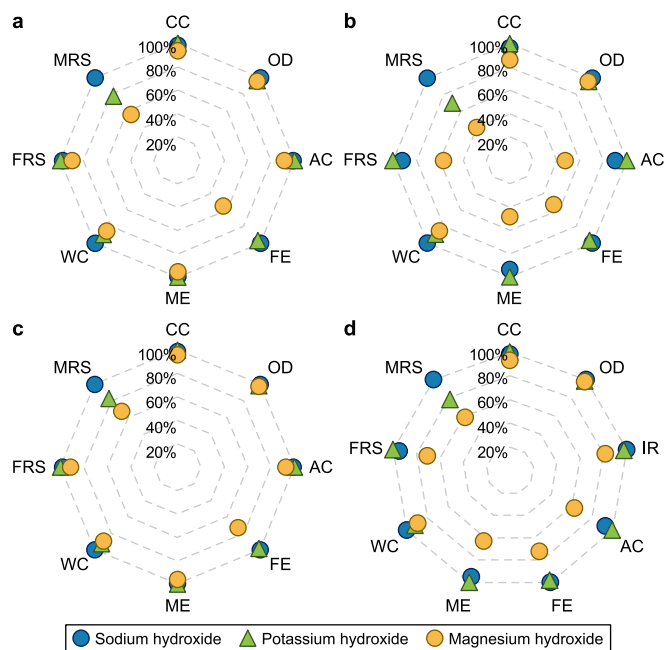


Fig. 5. Sensitivity analysis for the chemicals used during the operation of the fermenter to control pH. **a**, 1 t of valorized waste, scenario sewage sludge (SS), and considering the baseline substrate transportation; **b**, 1 t of valorized waste, scenario SS and without substrate transportation; **c**, 1 t of valorized waste, scenario food waste (FW) and considering the baseline substrate transportation; **d**, 1 t of valorized waste, scenario FW and without substrate transportation. CC: Climate change; OD: Ozone depletion; AC: Acidification; FE: Freshwater eutrophication; ME: Marine eutrophication; WC: Water consumption; FRS: Fossil resource scarcity; MRS: Mineral resource scarcity.

3.5. Sensitivity analysis for transportation

Based on the results shown in Fig. 4a, major differences can be found between the categories of CC, AC, ME, and FRS of all the scenarios proposed for analysis. When comparing the average distance assumed for goods by the Eurostat database and the optimum estimated for Galicia, a reduction of about 0.07–41.3% (WC and ME, respectively) is observed. Regarding CC, the decrease in the environmental impact of the complete treatment system is almost 26%. However, optimizing the distance is not as effective as selecting a truck with a low environmental impact, comparable to the scenario with the minimum distance. These two scenarios represented 11% (ME) and 99% (WC) of the baseline scenario for the distance between the Eurostat database and the municipal waste collection truck. Regarding CC, the representativeness was 44%.

The results of Fig. 4b align with those of Fig. 4a. In this case, the impact decrease from the baseline to the optimum scenario varied in the range of 0.09–57.8% (WC and ME as before), and CC had an impact reduction of about 28%.

3.6. Sensitivity analysis for chemicals

The use of NaOH has proven to have one of the strongest environmental impacts, along with the feedstock transportation to the facility (already stated in Sections 3.3 and 3.4). The sensitivity analysis results for the chemicals can be seen in Fig. 5. The outcomes are shown for the cradle-to-gate analysis (transportation of SS or FW included) and for a study in which only biorefinery-related impacts were incorporated. In this way, the results are also intended to guide facility managers.

KOH is a slightly better alternative to NaOH. Four categories improve within a range of 3–29% (for FE and MRS) while the other four worsen to a difference of 1.8%. Mg(OH)₂ is the option that may be used to substitute NaOH in the process. The process improves in all selected categories with a minimum improvement of 4.3% (for ME). Without transportation, the same categories improve up to 93%, and only OD is consistent for both system boundaries (around 4–5%).

3.7. Comparison with other processes from the literature

To compare the results obtained in this research with those of others in the literature, the environmental impact results were re-estimated and expressed in other product-based functional units used in publications found in the systematic literature review (more information in Supplementary Materials). All of them are summarized in Table 3.

However, one of the main problems when comparing LCA results is the large diversity of technical and methodological assumptions (i.e., system boundaries) adopted by the LCA practitioner. For example, in the production of acetic acid from SS, the CC impact of the treatment facility is 23.25 kg CO₂eq per kg acetic acid produced. Nevertheless, there is multifunctionality, which implies that the other two VFAs are also manufactured (propionic and butyric acid).

Because of this, the standalone production of acetic acid results in 20.03 kg CO₂eq per kg acetic acid produced, considering a mass allocation. This result is even smaller when the transportation problem (described in previous sections) is overcome: 8.56 kg CO₂eq per kg acetic acid produced. This indicates that the environmental viability of the biorefinery depends not only on the technology but also on the availability of feedstock and the distance for its supply.

If only the impacts of section S1 (pretreatment) and S2 (fermentation) were considered, the production of acetic acid for

Table 3
Comparison of the results of this research with literature for the climate change (CC) category.

Type of impact approach	SS	FW	SS (no transportation)	FW (no transportation)	Petro-based literature	Bio-based literature
Waste valorization						
Impact of acetic acid production per kg of waste (kg CO ₂ eq)	260.70	217.77	111.44	124.31	-	Between -0.171 and -0.695 kg CO ₂ eq [46]
Impact of butyric acid production per kg waste (kg CO ₂ eq)	33.47	92.06	14.31	52.55		14.6–15.9 kg CO ₂ eq [24] ¹
Impact of propionic acid production per kg waste (kg CO ₂ eq)	8.45	93.84	3.61	53.56		570 kg CO ₂ eq [19]
Total, impact per kg waste (kg CO ₂ eq)	302.62	403.68	129.36	230.42		
Volatile fatty acids production						
Impact of acetic acid production per kg of VFAs (kg CO ₂ eq)	15.84	5.22	6.77	2.98	-	0.186 kg CO ₂ eq [26]
Impact of butyric acid production per kg VFAs (kg CO ₂ eq)	2.03	2.21	0.87	1.26		
Impact of propionic acid production per kg VFAs (kg CO ₂ eq)	0.51	2.25	0.22	1.28		
Total, impact per kg VFAs (kg CO ₂ eq)	18.39	9.68	7.86	5.53		
Acetic acid production						
Impact of acetic acid production per kg of acetic acid (kg CO ₂ eq)	20.03	9.63	8.56	5.50	1.50 kg CO ₂ eq [47] and 2.50 kg CO ₂ eq [48,49]	6.03 kg CO ₂ eq [24] ¹
Impact of butyric acid production per kg acetic acid (kg CO ₂ eq)	2.57	4.07	1.10	2.32		4.41–10.95 kgCO ₂ eq [50]
Impact of propionic acid production per kg acetic acid (kg CO ₂ eq)	0.65	4.15	0.28	2.37		
Total, impact per kg acetic acid (kg CO ₂ eq)	23.25	17.85	9.94	10.19		
Butyric acid production						
Impact of acetic acid production per kg of butyric acid (kg CO ₂ eq)	156.03	22.78	66.70	13.01	-	0.327–0.727 kg CO ₂ eq [51]
Impact of butyric acid production per kg butyric acid (kg CO ₂ eq)	20.03	9.63	8.56	5.50		6.89–8.23 kg CO ₂ eq [52] ³
Impact of propionic acid production per kg butyric acid (kg CO ₂ eq)	5.06	9.82	2.16	5.60		
Total, impact per kg butyric acid (kg CO ₂ eq)	181.12	42.23	77.42	24.11		
Propionic acid production						
Impact of acetic acid production per kg of propionic acid (kg CO ₂ eq)	617.72	22.35	264.06	12.76	4.40 kg CO ₂ eq [49]	0.86 kg CO ₂ eq [25] ²
Impact of butyric acid production per kg propionic acid (kg CO ₂ eq)	79.31	9.45	33.90	5.39		
Impact of propionic acid production per kg propionic acid (kg CO ₂ eq)	20.03	9.63	8.56	5.50		
Total, impact per kg propionic acid (kg CO ₂ eq)	717.06	41.44	306.52	23.65		

Notes: 1. Dairy wastewater; 2. Synthetic wastewater, 3. Wheat straw.

the proposed process in this research would have an impact of 1.61 kg CO₂eq, thus making VFA production sufficiently competitive if the downstream stages improve environmental performance. For a feedstock such as FW, with a significantly higher yield for VFAs production, the global warming potential of these two stages would be 0.61 kg CO₂eq per kg acetic acid produced. This implies that, when using SS as feedstock, the downstream accounts for a total of 6.95 kg CO₂eq per kg acetic acid of the carbon footprint of the process. This is a value in line (4.41–10.95 kg CO₂eq) with the work of Petrescu & Cormos [50], who analyzed the acetic acid concentration from fermentation using isopropyl acetate and isopropanol mixture by thermally coupled process or by double effect distillation process. However, the LCA of these authors focused on the purification stage rather than the fermentation. On the other hand, Elginoz et al. [24] approached their study by considering only the fermentation of wastewater, and VFAs purification was not included. The results indicated an emission of 6.03 kg CO₂eq per kg acetic acid produced, which is higher than the results achieved for sections S1 and S2. This could be attributed, as already seen by the comparison between SS and FW, to the higher fermentation yield achieved by more biodegradable feedstocks. This conclusion can also be supported by the result achieved by Gracia et al. [26], who performed an LCA to treat SS by fermentation and the production of

VFAs. In contrast with Elginoz et al. [24], the outcome of Gracia et al. [26] (shown in Table 3) was below the 1.61 kg CO₂eq per kg acetic acid obtained for the S1 and S2 sections of the modelled Galician VFAs facility.

Fermentation seems to be a better solution than other technologies for producing VFAs from biomass. For example, Ahn et al. [19] reported a value of 570 kg CO₂eq per kg waste for the biomass fractionation of white birch, which is significantly higher than the results for SS (129.36 kg CO₂eq per kg waste) and FW (230.42 kg CO₂eq per kg waste) obtained by a fermentation process manufacturing commercial grade VFAs (with purification). Concerning the production of VFAs of fossil origin, petrochemical routes may have an impact representing 18–30% of the bio-based fermentation process (at least for acetic acid and SS feedstock). However, this comparison is not entirely fair since only the so-called “product approach” of the LCA was considered. A more unbiased bio-based vs. petrochemical benchmarking should have also incorporated the treatment of SS or FW, which is happening simultaneously in the bio-based fermentative process. Therefore, future studies should look at broader system boundaries and create interconnections within the different stages of a value chain.

Using fermentation to obtain other products, such as hydrogen, results in a carbon footprint of between 6.60 and 16.29 kg CO₂eq

per kg H₂ when valorizing lignocellulosic biomass [53]. Other authors, such as Reaño [54], have reported 10.92 kg CO₂eq per kg H₂ using the same technology but with rice husk as feedstock. Although it seems that producing VFAs is in line in terms of contribution to climate than the production of hydrogen (an energetic carrier) with the same technology, much higher results (818 kg CO₂eq per kg H₂) have also been found for hydrogen when treating palm oil effluent [55].

4. Conclusions

On the road to a more environmentally friendly biorefinery design with waste streams for VFAs production, the following key aspects must be considered: feedstock selection, resource consumption during process operation and the facility's location.

The selection of the feedstock seems to play an important role. Choosing between food waste and sewage sludge is not a straightforward decision since using food waste leads to a smaller footprint per unit product, but sewage sludge processing is better in terms of waste treatment capacity (i.e., the mass weight of waste influent). This is due to the proven higher anaerobic biodegradability of food waste, which translates into higher product yield and quantity. However, treating food waste also requires a greater demand for chemicals (i.e., the polyelectrolyte in solid–liquid separations) compared to sewage sludge.

Regarding resource consumption, the impact can be reduced by replacing NaOH with KOH (reduction of 29%), as this is the critical element in the process. Finally, the facility's location must be chosen by optimizing distances and should include an appropriate selection of the type of truck used for the waste transportation. This is because there is a potential for environmental impact improvement in the range of 26–53%.

The comparison of the VFAs biorefinery with other results in the literature seems to indicate that the competitiveness of the process depends largely on the impact of the purification steps rather than the fermentation. The carbon footprint aligns with other VFAs bio-based processes, but future research should demonstrate its feasibility compared to petrochemical processes and consider waste management.

CRedit authorship contribution statement

Ander Castro-Fernandez: Writing - Original Draft, Visualization, Investigation, Formal Analysis. **Sofia Estévez:** Writing - Original Draft, Visualization, Methodology, Investigation, Formal Analysis. **Juan M. Lema:** Writing - Review & Editing, Validation, Supervision. **Antón Taboada-Santos:** Writing - Review & Editing, Validation, Supervision. **Gumersindo Feijoo:** Writing - Review & Editing, Validation, Supervision. **María Teresa Moreira:** Writing - Review & Editing, Validation, Supervision.

Declaration of competing interest

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Appendix. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ese.2024.100518>.

References

- [1] Eurostat, Waste statistics. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Waste_statistics#Total_waste_generation, 2024. (Accessed 7 November 2024).
- [2] Eurostat, Sewage sludge production and disposal from urban wastewater (in dry substance (d. s)). https://ec.europa.eu/eurostat/databrowser/view/ten00030_custom_13649763/default/table?lang=en, 2024. (Accessed 7 November 2024).
- [3] European Compost Network, Bio-waste in Europe. <https://www.compostnetwork.info/policy/biowaste-in-europe/>, 2024. (Accessed 2 July 2024).
- [4] Eurostat, Sewage sludge production and disposal from urban wastewater (in dry substance (d. s)). <https://ec.europa.eu/eurostat/databrowser/view/ten00030/default/table?lang=en>, 2024. (Accessed 2 July 2024).
- [5] R. Soloha, L.K. Lukasa, E. Dace, Estimation and bio-valorisation of food industry by-products in Northern Europe, Biomass Convers Biorefin (2024), <https://doi.org/10.1007/s13399-024-05423-6>.
- [6] P. Pal, J. Nayak, Acetic acid production and purification: critical review towards process intensification, Separ. Purif. Rev. 46 (2017) 44–61, <https://doi.org/10.1080/15422119.2016.1185017>.
- [7] G. Merli, A. Becci, A. Amato, F. Beolchini, Acetic acid bioproduction: the technological innovation change, Sci. Total Environ. 798 (2021) 149292, <https://doi.org/10.1016/j.scitotenv.2021.149292>.
- [8] The Observatory of Economic Complexity, HS Icon Butyric acids, valeric acids, their salts & esters. <https://oec.world/en/profile/hs/butyric-acids-valeric-acids-their-salts-esters>, 2024. (Accessed 2 July 2024).
- [9] A. Naresh-Kumar, G.-B. Kim, A. Muhorakeye, S. Varjani, S.-H. Kim, Biopolymer production using volatile fatty acids as resource: effect of feast-famine strategy and lignin reinforcement, Bioresour. Technol. 326 (2021) 124736, <https://doi.org/10.1016/j.biortech.2021.124736>.
- [10] S. Agnihotri, D.-M. Yin, A. Mahboubi, T. Sapmaz, S. Varjani, W. Qiao, D.Y. Koseoglu-Imer, M.J. Taherzadeh, A glimpse of the World of volatile fatty acids production and application: a review, Bioengineered 13 (2022) 1249–1275, <https://doi.org/10.1080/21655979.2021.1996044>.
- [11] E.M. Research, Global acetic acid market report and forecast 2024-2032. <https://www.expertmarketresearch.com/reports/acetic-acid-market>, 2020. (Accessed 7 November 2024).
- [12] J.L. Martín-Espejo, J. Gandara-Loe, J.A. Odriozola, T.R. Reina, L. Pastor-Pérez, Sustainable routes for acetic acid production: traditional processes vs a low-carbon, biogas-based strategy, Sci. Total Environ. 840 (2022) 156663, <https://doi.org/10.1016/j.scitotenv.2022.156663>.
- [13] A. Vázquez-Fernández, M.E. Suárez-Ojeda, J. Carrera, Review about bioproduction of Volatile Fatty Acids from wastes and wastewaters: influence of operating conditions and organic composition of the substrate, J. Environ. Chem. Eng. 10 (2022) 107917, <https://doi.org/10.1016/j.jece.2022.107917>.
- [14] N. Ahmadi, K. Khosravi-Darani, A.M. Mortazavian, An overview of biotechnological production of propionic acid: from upstream to downstream processes, Electron. J. Biotechnol. 28 (2017) 67–75, <https://doi.org/10.1016/j.ejbt.2017.04.004>.
- [15] G. Deshmukh, H. Manyar, Production pathways of acetic acid and its versatile applications in the food industry, in: Biotechnological Applications of Biomass, IntechOpen, 2021, <https://doi.org/10.5772/intechopen.92289>.
- [16] J. Popp, Z. Lakner, M. Harangi-Rákos, M. Fári, The effect of bioenergy expansion: food, energy, and environment, Renew. Sustain. Energy Rev. 32 (2014) 559–578, <https://doi.org/10.1016/j.rser.2014.01.056>.
- [17] J.A. Kumar, S. Sathish, D. Prabu, A.A. Renita, A. Saravanan, V.C. Deivayanai,

- M. Anish, J. Jayaprakakar, O. Baigenzhenov, A. Hosseini-Bandegharai, Agricultural waste biomass for sustainable bioenergy production: feedstock, characterization and pre-treatment methodologies, *Chemosphere* 331 (2023) 138680, <https://doi.org/10.1016/j.chemosphere.2023.138680>.
- [18] Y.A. Hajam, R. Kumar, A. Kumar, Environmental waste management strategies and vermi transformation for sustainable development, *Environmental Challenges* 13 (2023) 100747, <https://doi.org/10.1016/j.envc.2023.100747>.
- [19] B. Ahn, C. Park, J.J. Liu, Y.S. Ok, W. Won, Maximizing the utilization of ligno-cellulosic biomass: process development and analysis, *Renew. Energy* 215 (2023) 119004, <https://doi.org/10.1016/j.renene.2023.119004>.
- [20] E. Budsberg, J.-T. Crawford, H. Morgan, W.S. Chin, R. Bura, R. Gustafson, Hydrocarbon bio-jet fuel from bioconversion of poplar biomass: life cycle assessment, *Biotechnol. Biofuels* 9 (2016) 170, <https://doi.org/10.1186/s13068-016-0582-2>.
- [21] D. da Silva Miranda, L.P. Martins, B.A. de S. Teles, I.L.C. Cunha, N. de A. Menezes, H. Sakamoto, L. Kulay, Alternative integrated ethanol, urea, and acetic acid processing routes employing CCU: a prospective study through a life cycle perspective, *Sustainability* 15 (2023) 15937, <https://doi.org/10.3390/su152215937>.
- [22] P. Fasahati, R. Dickson, C.M. Saffron, H.C. Woo, J.J. Liu, Seaweeds as a sustainable source of bioenergy: techno-economic and life cycle analyses of biochemical conversion pathways, *Renew. Sustain. Energy Rev.* 157 (2022) 112011, <https://doi.org/10.1016/j.rser.2021.112011>.
- [23] P. Tufvesson, A. Ekman, R.R.R. Sardari, K. Engdahl, L. Tufvesson, Economic and environmental assessment of propionic acid production by fermentation using different renewable raw materials, *Bioresour. Technol.* 149 (2013) 556–564, <https://doi.org/10.1016/j.biortech.2013.09.049>.
- [24] N. Elginöz, M. Atasoy, G. Finnveden, Z. Cetecioglu, Ex-ante life cycle assessment of volatile fatty acid production from dairy wastewater, *J. Clean. Prod.* 269 (2020) 122267, <https://doi.org/10.1016/j.jclepro.2020.122267>.
- [25] S. Dahiya, S. Lakshminarayanan, S. Venkata Mohan, Steering acidogenesis towards selective propionic acid production using co-factors and evaluating environmental sustainability, *Chem. Eng. J.* 379 (2020) 122135, <https://doi.org/10.1016/j.cej.2019.122135>.
- [26] J. Gracia, I. Cabeza, P. Acevedo, Life cycle analysis for the production of volatile fatty acids from wastewater treatment plant sludge, *Cogent Eng* 11 (2024), <https://doi.org/10.1080/23311916.2024.2335846>.
- [27] F. Morgan-Sagastume, S. Heimersson, G. Laera, A. Werker, M. Svanström, Techno-environmental assessment of integrating polyhydroxyalkanoate (PHA) production with services of municipal wastewater treatment, *J. Clean. Prod.* 137 (2016) 1368–1381, <https://doi.org/10.1016/j.jclepro.2016.08.008>.
- [28] L. Vogli, S. Macrelli, D. Marazza, P. Galletti, C. Torri, C. Samorì, S. Righi, Life cycle assessment and energy balance of a novel polyhydroxyalkanoates production process with mixed microbial cultures fed on pyrolytic products of wastewater treatment sludge, *Energies* 13 (2020) 2706, <https://doi.org/10.3390/en13112706>.
- [29] A.S.S. Pinto, L.J. McDonald, R.J. Jones, J. Massanet-Nicolau, A. Guwy, M. McManus, Production of volatile fatty acids by anaerobic digestion of biowastes: techno-economic and life cycle assessments, *Bioresour. Technol.* 388 (2023) 129726, <https://doi.org/10.1016/j.biortech.2023.129726>.
- [30] T. Soleymani Angili, K. Grzesik, E. Salimi, M. Loizidou, Life cycle analysis of food waste valorization in laboratory-scale, *Energies* 15 (2022) 7000, <https://doi.org/10.3390/en15197000>.
- [31] N. Elginöz, K. Khatami, I. Owusu-Agyeman, Z. Cetecioglu, Life cycle assessment of an innovative food waste management system, *Front. Sustain. Food Syst.* 4 (2020), <https://doi.org/10.3389/fsufs.2020.00023>.
- [32] A. Castro-Fernandez, L. Rodríguez-Hernández, C.M. Castro-Barros, J.M. Lema, A. Taboada-Santos, Scale-up and economic assessment of volatile fatty acids production from food waste, *Biomass Bioenergy* 182 (2024) 107112, <https://doi.org/10.1016/j.biombioe.2024.107112>.
- [33] Y. Liu, H. Yuan, N. Zhu, Accelerated stabilization of high solid sludge by thermal hydrolysis pretreatment in autothermal thermophilic aerobic digestion (ATAD) process, *J. Environ. Manag.* 318 (2022) 115615, <https://doi.org/10.1016/j.jenvman.2022.115615>.
- [34] T.L. Hansen, J. la Cour Jansen, H. Spliid, Å. Davidsson, T.H. Christensen, Composition of source-sorted municipal organic waste collected in Danish cities, *Waste Management* 27 (2007) 510–518, <https://doi.org/10.1016/j.wasman.2006.03.008>.
- [35] K. Khatami, M. Atasoy, M. Ludtke, C. Baresel, Ö. Eyce, Z. Cetecioglu, Bioconversion of food waste to volatile fatty acids: impact of microbial community, pH and retention time, *Chemosphere* 275 (2021) 129981, <https://doi.org/10.1016/j.chemosphere.2021.129981>.
- [36] APHA, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, 2012.
- [37] A. Castro-Fernandez, A. Taboada-Santos, S. Balboa, J.M. Lema, Thermal hydrolysis pre-treatment has no positive influence on volatile fatty acids production from sewage sludge, *Bioresour. Technol.* 376 (2023) 128839, <https://doi.org/10.1016/j.biortech.2023.128839>.
- [38] F. Battista, N. Frison, P. Pavan, C. Cavinato, M. Gottardo, F. Fatone, A.L. Eusebi, M. Majone, M. Zeppilli, F. Valentino, D. Fino, T. Tommasi, D. Bolzonella, Food wastes and sewage sludge as feedstock for an urban biorefinery producing biofuels and added-value bioproducts, *Journal of Chemical Technology & Biotechnology* 95 (2020) 328–338, <https://doi.org/10.1002/jctb.6096>.
- [39] Instituto Nacional de Estadística, Población por comunidades y ciudades autónomas y tamaño de los municipios, <https://www.ine.es/jaxiT3/Datos.htm?t=equals;2915>, 2024. (Accessed 2 July 2024).
- [40] ISO, ISO 14040:2006. Environmental management — life cycle assessment — principles and framework. <http://www.cscs.es/uploads/2016328/20160328110518251825.pdf>, 2006. (Accessed 29 September 2021).
- [41] ISO, ISO 14044:2006. Environmental management — life cycle assessment — requirements and guidelines. <https://www.iso.org/standard/38498.html>, 2006. (Accessed 17 January 2023).
- [42] IPCC, Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, vol. 5, 2019 chapter 6., 2019, https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/5_Volume5/19R_V5_6_Ch06_Wastewater.pdf. (Accessed 2 July 2024).
- [43] G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz, B. Weidema, The ecoinvent database version 3 (part I): overview and methodology, *Int. J. Life Cycle Assess.* 21 (2016) 1218–1230, <http://link.springer.com/10.1007/s11367-016-1087-8>. (Accessed 25 December 2022).
- [44] Eurostat, Road freight transport by type of operation and type of transport (t, tkm, vehicle-km) - annual data. https://ec.europa.eu/eurostat/databrowser/view/road_go_ta_tott/default/table?lang=en, 2024. (Accessed 2 July 2024).
- [45] Mivalt, Dewatering screw press vs. centrifuge: energy consumption, durability and noise level comparison. <https://www.mivalt.cz/en/news/dewatering-screw-press-vs-centrifuge-energy-consumption-durability-and-noise-level-comparison>, 2024. (Accessed 3 July 2024).
- [46] J.-L. Gálvez-Martos, S. Greses, J.-A. Magdalena, D. Iribarren, E. Tomás-Pejó, C. González-Fernández, Life cycle assessment of volatile fatty acids production from protein- and carbohydrate-rich organic wastes, *Bioresour. Technol.* 321 (2021) 124528, <https://doi.org/10.1016/j.biortech.2020.124528>.
- [47] J.D. Medrano-García, R. Ruiz-Femenia, J.A. Caballero, Revisiting classic acetic acid synthesis: optimal hydrogen consumption and carbon dioxide utilization, 145–150, <https://doi.org/10.1016/B978-0-12-818634-3.50025-4>, 2019.
- [48] E. Budsberg, R. Morales-Vera, J.T. Crawford, R. Bura, R. Gustafson, Production routes to bio-acetic acid: life cycle assessment, *Biotechnol. Biofuels* 13 (2020) 154, <https://doi.org/10.1186/s13068-020-01784-y>.
- [49] CarbonCloud, Propionic acid, fossil based. <https://apps.carboncloud.com/climatehub/product-reports/id/143249778560>, 2024. (Accessed 3 July 2024).
- [50] L. Petrescu, C.-M. Cormos, Classical and process intensification methods for acetic acid concentration: technical and environmental assessment, *Energies* 15 (2022) 8119, <https://doi.org/10.3390/en15218119>.
- [51] A. Suazo, F. Tapia, G. Aroca, J. Quintero, Techno-economic and life cycle assessment of a small-scale integrated biorefinery for butyric acid production in Chile, *Fermentation* 10 (2023) 1, <https://doi.org/10.3390/fermentation10010001>.
- [52] I. Cámara-Salim, S. González-García, G. Feijoo, M.T. Moreira, Screening the environmental sustainability of microbial production of butyric acid produced from lignocellulosic waste streams, *Ind. Crops Prod.* 162 (2021) 113280, <https://doi.org/10.1016/j.indcrop.2021.113280>.
- [53] A. Mehmeti, A. Angelis-Dimakis, G. Arampatzis, S. McPhail, S. Ulgiati, Life cycle assessment and water footprint of hydrogen production methods: from conventional to emerging technologies, *Environments* 5 (2018) 24, <https://doi.org/10.3390/environments5020024>.
- [54] R.L. Reaño, Assessment of environmental impact and energy performance of rice husk utilization in various biohydrogen production pathways, *Bioresour. Technol.* 299 (2020) 122590, <https://doi.org/10.1016/j.biortech.2019.122590>.
- [55] A. Akhbari, C.C. Onn, S. Ibrahim, Analysis of biohydrogen production from palm oil mill effluent using a pilot-scale up-flow anaerobic sludge blanket fixed-film reactor in life cycle perspective, *Int. J. Hydrogen Energy* 46 (2021) 34059–34072, <https://doi.org/10.1016/j.ijhydene.2021.07.186>.