

## Article

# Prefeasibility Analysis of Different Anaerobic Digestion Upgrading Pathways Using Organic Kitchen Food Waste as Raw Material

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**Abstract:** Anaerobic digestion (AD) is a widely applied technology for renewable energy generation using biogas as energy vector. The existing microbial consortium in this technology allows for the use of several types of biomass as substrates. A promising alternative for the production of high-value products (e.g., mixed volatile fatty acids–VFAs, hydrogen) is the use of modified AD. There are several techniques to achieve this objective by modifying the operating conditions of the process. The literature has described the best AD routes for generating renewable energy or high-value products based on specific substrate types and operating conditions. Few studies have reported the integral fraction valorization of the AD process applying the biorefinery concept. This article provides an analysis of the different routes that favor the production of energy carriers and high-value products involving key issues related to operating conditions and substrates. Moreover, AD is addressed through the biorefinery concept. Finally, a case study is presented where renewable energy and mixed VFAs are generated by applying the biorefinery concept in a number of proposed scenarios using organic kitchen food waste (OKFW) as feedstock. The case study involves an experimental and simulation stage. Then, the economic feasibility of the proposed scenarios is evaluated. In conclusion, AD is a promising and economically feasible technology to produce valuable products from several types of waste materials.



**Citation:** Agudelo-Patiño, T.; Ortiz-Sánchez, M.; Alzate, C.A.C. Prefeasibility Analysis of Different Anaerobic Digestion Upgrading Pathways Using Organic Kitchen Food Waste as Raw Material. *Fermentation* **2024**, *10*, 300. <https://doi.org/10.3390/fermentation10060300>

Academic Editor: Giulia Bozzano

Received: 9 May 2024

Revised: 30 May 2024

Accepted: 1 June 2024

Published: 5 June 2024



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**Keywords:** anaerobic digestion; bioenergy; high-value-added products; biorefinery; mixed VFAs

## 1. Introduction

In recent decades, anaerobic digestion (AD) as a means of producing energy has been of great interest due to the potential applications, the simplicity of the process, and the wide range of feedstocks that can be used (food waste, agricultural waste, sewage sludge). Energy production from AD increased by more than 90% between 2010 and 2018 and was successfully implemented in European countries, the United States, and some Latin American countries [1]. The different links are generally independent, and the reuse or waste transformation processes are not involved in the generation of new high-value products. Processes based on a circular economy consider a transformation model with an approach to economic growth that is aligned with sustainable economic and environmental development [2]. In this sense, the solid establishment of connections between the different links and actors of existing and emerging value chains (VC) and processes are key elements for the transition to a bio-based circular economy [3]. The organic waste conversion strategies practiced in industrialized countries include the conversion of waste into energy in industrial plants [4]. Among the alternatives to reduce these wastes, the upgrading of the food supply chain from the post-harvest stage is being considered [5]. Nevertheless, countries with underdeveloped sectors lack systems for appropriate waste management due to inefficient infrastructures, and a lack of policy frameworks and financing [2]. An alternative is the integrated use of organic waste generated at any stage of the food supply

chain to produce energy carriers or value-added products through easily implementable technologies such as AD [6]. AD has been applied to decompose organic wastes and produce renewable energy. The process involves a series of biochemical reactions produced by the action of a consortium of microorganisms [7]. The main product obtained from AD is biogas composed of methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), and impurities [8]. Biogas focusing on renewable energy production is the main pathway of AD. However, recent research studies have shown that AD could be designed to produce high-value products such as mixed volatile fatty acids, fertilizers, hydrogen [9]. Volatile fatty acids (VFAs) are carboxylic acids with a low molecular weight, containing between six or fewer carbon atoms, including acetic, propionic, iso-butyric, n-butyric, and iso-valeric acid, [10]. Mixed VFAs generated during the AD process can be separated into individual forms through techniques such as distillation, membrane separation, and liquid–liquid extraction, among others. Most of these methods have some disadvantages such as the coproduction of other products or extra process steps [11]. Consequently, different strategies have been evaluated to use mixed VFAs as substrates for the production of high-value products such as polyhydroxyalkanoates and biodiesel [12]. On the other hand, digestate (the wet residue generated in AD) is a mixture of partially degraded organic matter, microbial biomass, and inorganic compounds [13]. Digestates can contain high amount of undigested material, nutrients, and trace elements (i.e., N, P, K, Co, Fe, Se) [14]. Direct application of digestate to the soil is currently considered an economically attractive process [15]. During AD, most of the labile organic components are degraded, increasing the stability of the remaining organic matter in the digestate. Nevertheless, the prevalence of efficiency criteria for energy production (biogas) on an industrial scale can lead to a limited residence time of the material in the digester, producing a digestate that is not fully depleted in terms of readily degradable organic compounds [16]. The integral valorization of all fractions generated in the digestion process (products, by-products, and wastes) in a network of facilities leads to the biorefinery concept. A biorefinery is a complex system in which biomass is integrally processed or fractionated to obtain more than one product that may include bioenergy (i.e., direct energy), biofuels, chemicals, and high value-added compounds that can only be extracted from bio-based sources [17]. These characteristics have led to the evaluation of several valorization routes [18]. The biorefinery concept encompasses using all fractions generated during the AD process. Multiple production lines are possible from this process. Conventional anaerobic digestion can be performed to obtain biogas and extract valuable compounds from the remaining fractions. Likewise, modified anaerobic digestion (variation of operating conditions) can also be performed to promote other metabolic pathways and generate valuable compounds. Some possible production lines from the different fractions obtained in the process are shown in Figure 1. Generally, when lignocellulosic wastes (e.g., crop wastes) are used as feedstock, due to their complex structure, pretreatment steps are performed before digestion.

Several reviews focus on describing the best routes (based on operating conditions, substrate types, purification techniques, economic analysis, or environmental analysis) for AD regarding producing energy vectors and high-value products. However, the known analyses, so far, are of an isolated nature. The novelty of this article lies in highlighting the role of AD in the generation not only of renewable energy but also in the production of high-value products through the biorefinery concept. Then, this article provides a general review of the different routes that favor the production of energy carriers and high-value products involving key issues related to operating conditions, substrates, and applications. A case study is also presented where AD is assessed from a biorefinery perspective to produce biogas and mixed VFAs. Experimental and simulation stages are considered. In addition, the pre-feasibility of different scenarios is evaluated based on economic metrics.

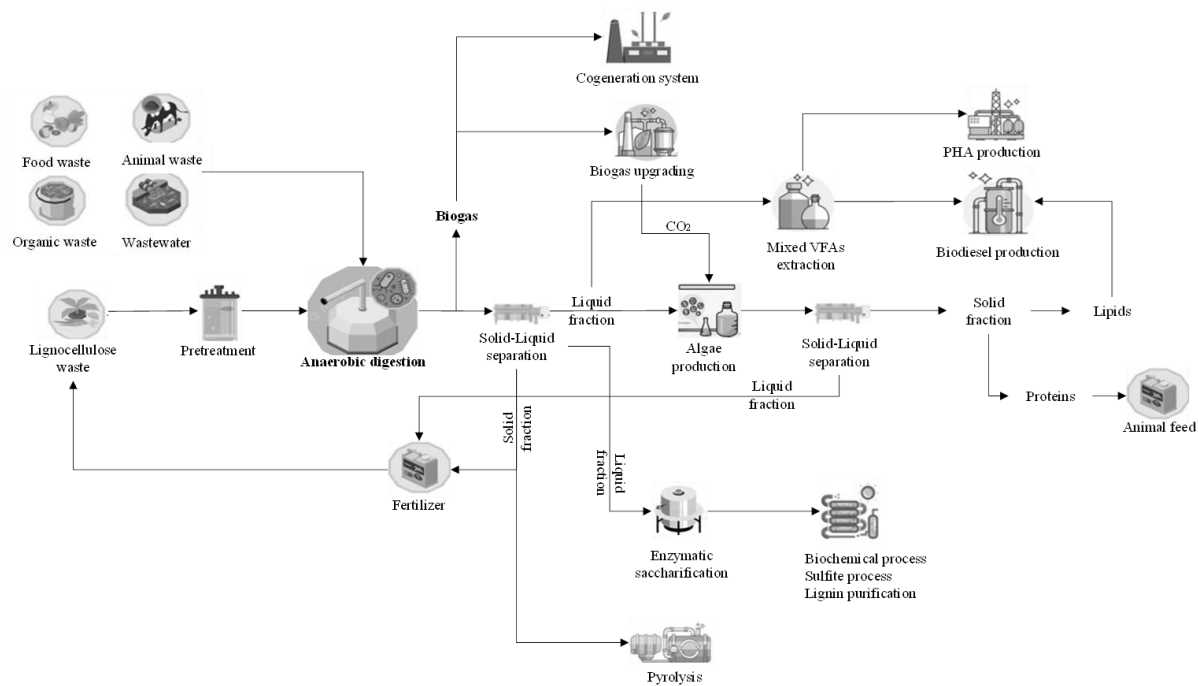


Figure 1. Schematic of an anaerobic biorefinery for producing bioenergy and bio-based products.

2. Overview of Anaerobic Digestion System

2.1. Biochemical Reactions and Steps

AD is a biological and degradative process where a substrate (organic waste) generates biogas without oxygen in the medium [7]. The AD process of biodegradable organic resources consists of four main stages, as follows: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (see in Figure 2). AD is a complex process involving several groups of bacteria and substrates, and takes place under strict anaerobic conditions to transform organic matter mainly into methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), and traces of hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), and other gases. Each degradation step is carried out by different microorganisms, acting in interrelation, that require different environmental conditions [19].

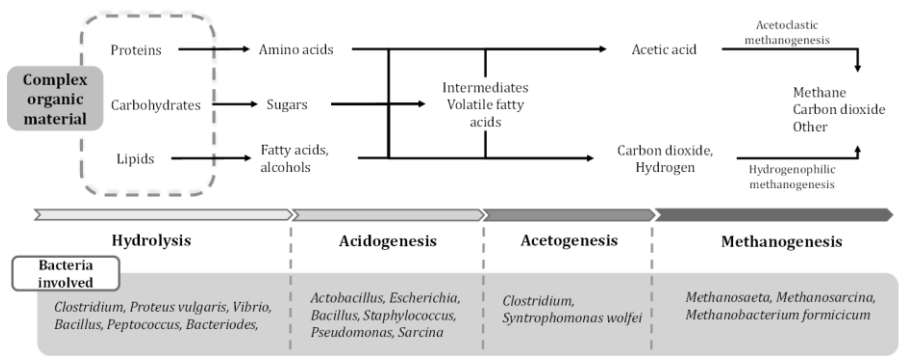


Figure 2. Stages of the AD process.

The first stage of the AD process is hydrolysis. In this stage, complex organic polymers are converted into simple soluble molecules. During the hydrolysis stage, lipids (fats) are converted into fatty acids, carbohydrates (polysaccharides) into simple sugars (monosaccharides), and proteins into amino acids. Different groups of bacteria carry out the hydrolysis step through the excretion of extracellular enzymes (see Table 1) [20]. Lipases convert lipids to long-chain fatty acids, proteases convert proteins to amino acids, and polysaccharides, such as cellulose, starch, and pectin, are hydrolyzed to monosaccharides by cellulases,

amylases, and pectinases, respectively. Generally, the hydrolysis of carbohydrates takes a few hours, but the degradation of proteins and lipids takes a few days [21].

In the second stage, the soluble compounds produced by hydrolysis diffuse into other bacterial cells (i.e., acidogenic bacteria). These compounds are converted into mixed VFAs, hydrogen, CO<sub>2</sub>, ethanol, and some organic nitrogen and sulfur compounds [22]. The predominant acids produced at this stage are acetic, propionic, butyric, and valeric acids [23]. The acetic acid formed in this stage is directly taken to the last stage, and the other products are taken to the third stage for further degradation by acetogens [24]. Alcohols and mixed VFAs can be decomposed into acetic acid and hydrogen in the acetogenesis stages. As these two processes are very rapid, a sudden drop in pH might occur. When AD of food waste is available, the process involves a high rate of hydrolysis, indicating that more of the substrate is available for the acidogenesis bacteria [25].

The third stage of the AD process corresponds to acetogenesis. In this stage, mixed VFAs having more than two carbon atoms (from the acidogenesis stage) are converted into acetic acids, hydrogen, and carbon dioxide by the action of acetogens [26].

**Table 1.** Chemical reactions and bacteria involved in the AD process [27,28].

| Stage          | Reactions                                                                                                                                                                                                                                                                                     | Process Conditions                                                                                                                                 | Involved Bacteria                                                                                                                                                                                                                 | Conversion                                                                                                                  |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| Hydrolysis     | $(C_6H_{10}O_5)_n + nH_2O \rightarrow n(C_6H_{12}O_6)$                                                                                                                                                                                                                                        | T: 25–30 °C; pH 5.2–6.8;<br>C/N ratio: 10–45;<br>Required C:N:P:S ratio:<br>500:15:5:3; facultative<br>microorganisms                              | <i>Clostridium</i> , <i>Proteus<br/>vulgaris</i> , <i>Vibrio</i> , <i>Bacillus</i> ,<br><i>Peptococcus</i> , <i>Bacteriodes</i> ,                                                                                                 | Carbohydrates-soluble<br>sugars.<br>Proteins-soluble peptides<br>and amino acids.<br>Lipids-fatty acids or<br>alcohols      |
| Acidogenesis   | $C_6H_{12}O_6 + H_2O \rightarrow CH_3COOH + 4H_2 + CO_2$<br>$C_6H_{12}O_6 + H_2 \rightarrow CH_3CH_2COOH + 2H_2O$<br>$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2$<br>$C_6H_{12}O_6 \rightarrow 2CH_3CH_2COH + 2CO_2$<br>$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$                | T: 25–30 °C; pH: 5.2–6.5;<br>C/N ratio: 10–45;<br>Generation time: 24–36 h;<br>facultative<br>microorganisms                                       | <i>Actobacillus</i> , <i>Escherichia</i> ,<br><i>Bacillus</i> , <i>Staphylococcus</i> ,<br><i>Pseudomonas</i> , <i>Sarcina</i> ,<br><i>Desulfovibrio</i> ,<br><i>Streptococcus</i> , <i>Veillonell</i> ,<br><i>Desulforomonas</i> | Amino acids-fatty acids,<br>acetate, and others.<br>Sugars-intermediary<br>fermentation products                            |
| Acetogenesis   | $CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + 2H_2$<br>$2CH_3CH_2COH + 2CO_2 \rightarrow 2CH_3COOH + CH_4$<br>$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + 3H_2 + CO_2$<br>$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$<br>$CH_3CHOHCOOH + H_2O \rightarrow CH_3COOH + CO_2 + 2H_2$ | Generation time: 80–90 h                                                                                                                           | <i>Clostridium</i> ,<br><i>Syntrophomonas wolfeii</i> ,<br><i>Syntrophomonas wolfeii</i>                                                                                                                                          | Higher fatty acids or<br>alcohols- hydrogen and<br>acetate.<br>Volatile fatty acids and<br>alcohols- acetate or<br>hydrogen |
| Methanogenesis | $CH_3COOH \rightarrow CH_4 + CO_2$<br>$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$                                                                                                                                                                                                                  | Mesophilic: 32–42 °C;<br>Thermophilic: 50–58 °C;<br>pH: 6.0–8; C/N ratio:<br>20–30, Generation time:<br>5–16 d; Strict anaerobes<br>microorganisms | <i>Methanosaeta</i> ,<br><i>Methanosarcina</i> ,<br><i>Methanobacterium<br/>formicum</i> ,<br><i>Methanobrevibacterium</i>                                                                                                        | Acetate-methane and<br>carbon dioxide.<br>Hydrogen and carbon<br>dioxide- methane                                           |

In the last stage, methanogenic bacteria (methanogens) produce methane by consuming acetic acid, hydrogen, and carbon dioxide. Almost 70% of methane is formed from acetic acids by the decarboxylation of acetate (acetotrophic methanogens) [29]. In this type of methanogenesis, acetic acid is decomposed into a carbon dioxide molecule and a methyl group. CO is gradually oxidized and coincides with the release of electrons necessary to reduce the methyl group to methane [30]. The remaining 30% of methane is formed from reducing carbon dioxide with the participation of hydrogen as an electron donor (hydrogenotrophic methanogens) [27].

## 2.2. Microorganisms Involved in Anaerobic Digestion

The conversions of complex organic compounds into CH<sub>4</sub> and CO<sub>2</sub> are possible due to the cooperation of four different groups of microorganisms. These microorganisms can be counted among primary fermentation bacteria, secondary fermentation bacteria (syntrophic and acetogenic bacteria), and two types of methanogens belonging to the *Archaea* domain. These microorganisms are found in the natural environment and perform various functions during the anaerobic degradation of waste. Cooperation in the population of microorganisms allows for the synthesis of certain products later used as food by another group of bacteria [31]. Interspecific transfer of hydrogen during the acetogenic stage

allows for the growth of syntrophic bacteria (a species living on the metabolic products of another species such as *Syntrophomonas* and *Syntrophospora*). These microorganisms oxidize compounds such as propionate and butyrate [32]. Syntrophic bacteria cannot grow in the form of pure cultures and are only accompanied by microorganisms that use the hydrogen produced by them, for example, mutagenic archaeons [33]. Therefore, syntrophy is an essential process during the stages of digestion, in which the decomposition of a compound occurs by the participation of two or more microorganisms; none of these can use this compound separately. Methanogenic archaeons use the  $\text{CH}_3\text{COOH}$  and  $\text{H}_2$  produced by these bacteria to produce methane. Methanogens process a limited amount of simple organic substrates, the most important of which are  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2$ , and  $\text{CO}_2$  [34]. De Vrieze et al. [35] analyzed the effect of four different inoculums on the methane production potential. The authors reported a high free-ammonia concentration in the mainly animal manure inoculum and increased residual VFA concentrations in the energy crops and manure inoculum, indicating an unstable methanogenic community.

### 2.3. Parameters in Anaerobic Digestion

#### 2.3.1. Feedstock

Any source of organic matter is considered suitable for being implemented in AD [36]. The preference lies in using raw materials of residual origin. This contributes to mitigating waste and adverse effects (economic, social, and environmental) [37]. In addition, conflicts related to using crops for food consumption and generating high-value products are avoided [38]. The most solid wastes used in AD include agricultural, livestock, sewage sludge, municipal solid waste (organic fraction), and food wastes. For liquid wastes, wastewater, and wastes from the agro-industrial, chemical, food processing, and pharmaceutical industries have been used [39]. The biochemical characteristics of the raw material to produce the previously mentioned products should favor the development and microbial activity of the system.

Lignocellulosic waste comprises mainly crop residues. These residues are difficult for microorganisms to digest due to the chemical composition (high cellulose, hemicellulose, and lignin content) [40]. Then, the residues should be submitted to previous processes (pretreatments) in order to favor hydrolysis [41]. Moreover, due to the high C/N ratio, several studies have evaluated the co-digestion processes of lignocellulosic waste and other organic materials.

The constant economic growth, urbanization, industrialization, and accelerated obsolescence of products and consumer wastes have led to a progressive increase in municipal solid waste (MSW) [42]. MSW consists mainly of food waste, paper and cardboard, yard trimmings, wood, plastic, metal, and glass [11]. Almost 60% of MSW is composed of organic matter, followed by paper and cardboard (13%), and plastics (10%) [43]. Organic wastes are a unique case within biomass, where valorization into renewable energy and high-value products through AD represents one of the most attractive processes for utilization [44].

Generally, in most countries, livestock farming is in constant development and manure is mostly used as fertilizer. Nevertheless, manure abundance exceeds the demand for fertilizer production [45]. Several studies have been put forward to use animal manure as a substrate to be implemented in AD [46,47]. Manure mono-digestion generates low biogas yields due to nutrient imbalance and ammonia inhibition (low C/N ratio). Livestock manure generally contains high nitrogen content. Examples include chicken manure (1.03%), cow manure (0.35%), fresh goat manure (1.01%), and pig manure (0.24%) [48]. Co-digestion techniques using animal manure with other organic matter have been proposed to solve the aforementioned limitations [49,50]

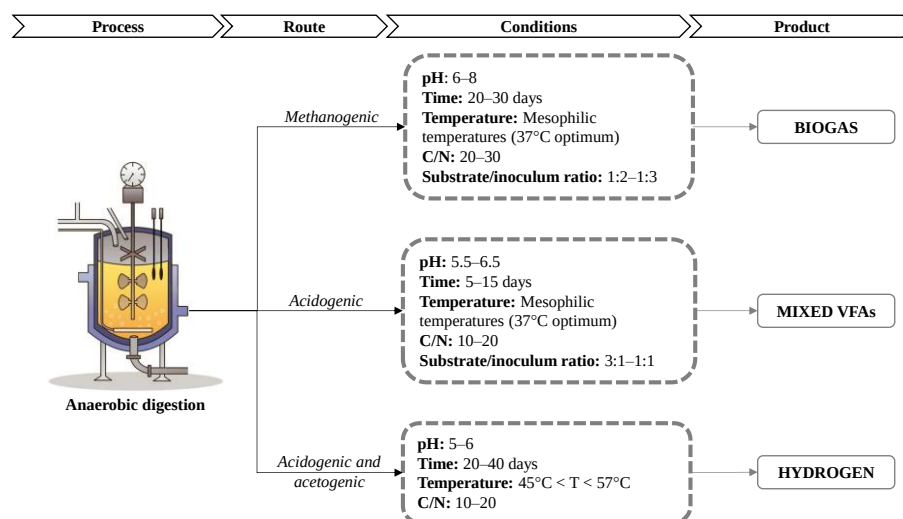
#### 2.3.2. Inoculum

As mentioned above, AD of organic matter is carried out by a consortium of microorganisms in sequential stages, resulting in a synergistic action [51]. The quality and quantity of inoculum added to the digestion process are key factors determining the biogas and

digestate quality. In addition, selecting the waste-to-inoculum ratio is crucial, as well as evaluating the anaerobic biodegradability of solid wastes [52]. Thus, several inoculums have been used for biogas production. For instance, Forster et al. [53] determined swine wastewater, rumen, and sewage sludge as promising inoculums for biogas production due to the high methanogenic bacteria content.

### 2.3.3. Operational Parameters

Several studies have evaluated the effects of operating conditions, such as pH, temperature, organic loading rate, retention time, substrate, and inoculum, on the AD process for generating energy and high-value products [54]. In this section, the main differences in the operating conditions to favor some routes of the AD process are described. Figure 3 shows the main differences between the operating conditions for the analyzed routes.



**Figure 3.** Process to obtain different products of the AD.

Small changes in pH levels affect the anaerobic process. Methanogenic microorganisms are more susceptible to pH variations than other microorganisms in the anaerobic microbial community [55]. The different bacterial groups in the AD process have optimal activity levels at an approximately neutral pH [56]. The pH value in the biodigester not only determines the biogas production but also the composition. Low pH values reduce the activity of methanogenic microorganisms, causing the accumulation of acetic acid and hydrogen. Consequently, propionic-acid-degrading bacteria might be severely inhibited, causing the excessive accumulation of mixed VFAs [57]. The optimum pH for hydrolysis and acidogenesis is in the range of 5.2 to 6.3. Most acidogens do not survive at either a very low pH (<pH 3) or a very high pH (>pH 12) [58].

The AD process is strongly temperature-dependent. The reaction rate of biological processes depends on the growth rate of the microorganisms involved and the medium temperature [59]. As the temperature increases, the growth rate of the microorganisms increases, and the digestion process is accelerated, resulting in higher biogas yields [56]. Nevertheless, abrupt temperature variations in the biodigester can generate destabilization of the process. Anaerobic microorganisms can tolerate the following three temperature ranges: psychrophilic (below 25 °C, not very applicable), mesophilic (between 25 and 45 °C, most commonly used), and thermophilic (between 45 and 65 °C). Temperature affects mixed-VFA production because of the effect on microbial growth. Many acidogens grow optimally at mesophilic temperatures. According to studies in the literature, increasing the temperature to 45 °C for biohydrogen production improves the production of H<sub>2</sub> from potato peel waste [60]. Likewise, a higher temperature of 57 °C promotes the maximum hydrogen production from palm oil mill effluent [61].

Hydraulic retention time (HRT) refers to the time the substrate is stored in the digester [62]. Generally, the HRT varies between 10 and 40 days for mesophilic microorganisms. For thermophilic microorganisms, the retention can last 14 days [63]. Short retention times are preferred for hydrogen-producing bacteria since VFAs, and hydrogen are produced in the exponential phase and alcohols in the stationary phase. As methanogenic bacteria consume hydrogen to produce methane and carbon dioxide, a higher hydrogen yield is obtained when inhibited. Conversely, there is a decrease in methane production by methanogenic bacteria at short retention times [64].

Most organic matter is potentially applicable to AD processes [65]. The yield and quality of the final product might be influenced by the composition and nature of the feedstock. Carbon and nitrogen are the main energy sources and feed for forming new cells of methanogenic microorganisms. These microorganisms consume approximately 30 times more carbon than nitrogen, so the optimal ratio reported for these two elements is 30:1 [66]. The decomposition of organic matter with high carbon content (>35:1) occurs slowly because the multiplication and development of bacteria is low due to the absence of nitrogen, but the biogas production period is longer. On the other hand, with a C/N ratio lower than 8:1, bacterial (methanogenic) activity is inhibited due to the formation of excessive ammonium content, reducing the pH of the medium and consequently favoring the production of mixed VFAs.

#### *2.4. Products Derived from Anaerobic Digestion*

A promising alternative for the production of high-value products (e.g., mixed VFAs, hydrogen) is through the use of modified AD to minimize the release of carbon dioxide and methane [67]. There are several techniques to achieve this objective, mainly by changing the operating conditions of the process (pH, temperature, agitation speed, time, raw material, etc.) [4]. These techniques consist of inhibiting methane-producing microorganisms and favoring other routes or stages to the process. This means preventing the methanogenesis process from occurring to ensure that only the desired products are obtained in higher volumes [68].

##### *2.4.1. Biogas*

Biomass-to-energy conversion has been constantly increasing to reduce the environmental impact generated by exploiting and consuming non-renewable energy sources [69]. Biogas is generated in natural media or specific devices by biodegradation reactions of organic matter through the action of microorganisms in the absence of oxygen [70]. Currently, most methane consumption and utilization is derived from natural gas resources, but biomethane production from waste recovery approaches has increased significantly. The production potential has improved by 4% in 9 years (from 2010 to 2018) [71]. Developed countries use large-scale advanced plants to utilize biogas. Biogas is regularly applied to generate heat, power, and electricity. In addition, several industrial applications are being developed in biogas plants as a substitute for natural gas [72]. In the European Union and North America, biogas plants have been more developed than in other continents during the last 40 years. The main advantages of the units located in the aforementioned regions are industrial scale, energy efficiency, and a high level of complexity [73]. Biogas production from different feedstock is presented in Table 2.

Table 2. Results for biogas production from different feedstock.

| Biogas Production           |                                                                                                          |                               |                                                                                                                                            |      |
|-----------------------------|----------------------------------------------------------------------------------------------------------|-------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|------|
| Feed Stock                  | Operation Condition                                                                                      | Yield (m <sup>3</sup> /kg VS) | Comments                                                                                                                                   | Ref  |
| Potato waste                | pH: 7.64, TR: 35 days, T: 37 °C, Scale: CSTR reactor                                                     | 435.7                         | Gradually increasing the organic loading rate from 1.0 to 5.0 kg VS/m <sup>3</sup> -day improved methane yield.                            | [74] |
| Kitchen waste               | pH: 7.5, TR: 45 days, T: 35 °C, Scale: Laboratory                                                        | 179.8                         | The effect of different initial pH (6.0, 7.0, 7.5, and 8.0) on laboratory-scale AD of kitchen waste was investigated.                      | [75] |
| Food waste                  | pH: 7.1–7.5, TR: N.R, T: 35 °C, Scale: CSRT reactor                                                      | 344                           | The effects (temperature and substrate characteristics) on process stability and microbial community structure were studied.               | [76] |
| Food waste                  | pH: 6.8, TR: 302 days, T: 35 °C, Scale: Batch reactor                                                    | 388                           | The effects of organic loading rate (OLR) and temperature on the co-digestion of food waste and residual activated sludge were evaluated.  | [77] |
| Municipal food waste        | pH: 7.64, TR: 17.5 days, T: 37 °C, Scale: CSRT                                                           | 444.7                         | The yield and kinetic constants of mesophilic anaerobic reactors operated at increasing organic loading rates were evaluated.              | [78] |
| Fruits and vegetables waste | pH: 7.4, TR: 30 days, T: 35 °C, Scale: CSRT, co-digestion: slaughterhouse waste + manure: 11-8-7         | 320                           | The co-digestion process (slaughterhouse waste + manure) was evaluated to reduce the volatile solids content of fruit and vegetable waste. | [79] |
| Cow manure                  | pH: 7.5, TR: 38 days, T: 35 °C, Scale: CSRT, co-digestion of grass silage, sugar beet tops and oat straw | 188                           | A 1:4 ratio of manure to crop residues promotes biogas production.                                                                         | [19] |

Academic centers and governments have considered biogas production because of the potential to respond to different global challenges [80]. Moreover, biogas technologies enable industries to eliminate greenhouse gas (GHG) emissions and pollution from waste disposal. Due to their renewable nature, these technologies also provide a broad spectrum of energy utilization such as heat, electricity, and transportation. Another advantage of biogas production is the applicability in rural areas with limited access to energy sources [81]. Thus, the calorific value of biogas is estimated to be around 5300 kcal/m<sup>3</sup> and is associated with the methane content. The presence of inhibitors during the process (e.g., volatile fatty acids), and compounds such as CO<sub>2</sub> H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>O, N<sub>2</sub>, and siloxanes in the product, decreases the product yield and calorific value when compared to natural gas (see Table 3) [82].

Table 3. Composition of biogas and natural gas according to [83].

| Character           | Unit | AD Biogas | Natural Gas | Biogas Utilization Impact                                                 |
|---------------------|------|-----------|-------------|---------------------------------------------------------------------------|
| CH <sub>4</sub>     | %vol | 53–70     | 81–89       |                                                                           |
| CO <sub>2</sub>     | %vol | 30–50     | 0.67–1      | Decreasing calorific value, antiknock properties of engines and corrosion |
| N <sub>2</sub>      | %vol | 2–6       | 0.28–14     | Decreasing calorific value, antiknock properties of engines and corrosion |
| O <sub>2</sub>      | %vol | 0–5       | 0           | Corrosion, fooling in cavern storage, risk of explosion                   |
| H <sub>2</sub>      | %vol | N.R       | N.R         |                                                                           |
| Higher hydrocarbons | %vol | N.R       | 3.5–9.4     |                                                                           |

Table 3. Cont.

| Character        | Unit               | AD Biogas | Natural Gas | Biogas Utilization Impact                                               |
|------------------|--------------------|-----------|-------------|-------------------------------------------------------------------------|
| H <sub>2</sub> S | ppm                | 0–2000    | 0–2.29      | Corrosion, catalytic converter poison, emission, and health hazards.    |
| NH <sub>3</sub>  | ppm                | <100      | N.R         | Emission, anti-knock properties of engines and corrosion when dissolved |
| LHV              | MJ/Nm <sup>3</sup> | 23        | 40          |                                                                         |
| Density          | kg/Nm <sup>3</sup> | 1.1       | 0.84        |                                                                         |

LHV: Low heating value; N.R no report.

Biogas can be used as fuel. To comply with country-specific regulatory standards, several biogas upgrading methods have been developed [84]. Figure 4 shows some biogas upgrading technologies. To date, the most widely used technology is adsorption (water washing) [85]. Moreover, biogas has the potential to generate electricity in power plants where the most commonly used generation methods are internal combustion engines or gas turbines [86].

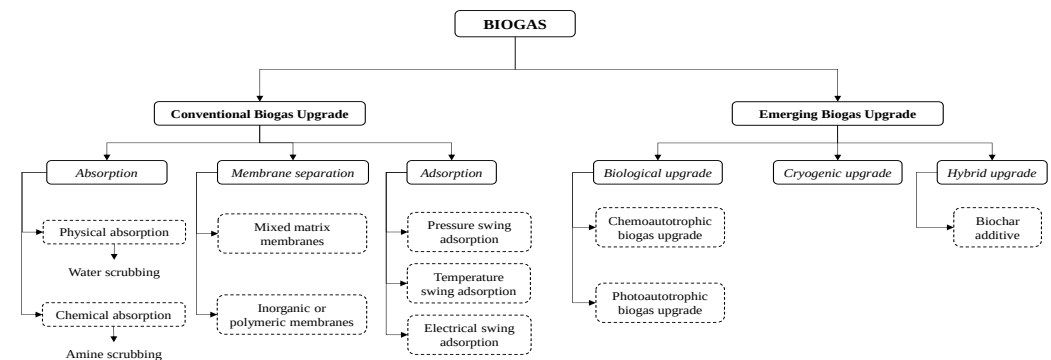


Figure 4. Biogas upgrading technologies.

#### 2.4.2. Hydrogen

The third stage of the digestion process (acetogenesis) plays a key role in biohydrogen production [87]. In this stage, the mixed VFAs are converted to acetate and hydrogen. When hydrogen production is promoted, the specific gas can be generated during treatment or after digestion [88]. Currently, about 85% of the hydrogen produced in the world is obtained from reforming fuels, and the remaining 15% is obtained through electrolysis or electrolysis of water. In 2019, the industry produced and consumed approximately 70 tons of hydrogen. Generally, the hydrogen produced currently is consumed in hydrocracking and desulfurization processes for the crude oil refining industry, or for ammonia production when combined with nitrogen in chemical industries [89]. Pure hydrogen is used in many applications and can be found in the production of many common industries. Hydrogen is also used in hydrogen fuel cells, producing energy for vehicles and other systems [90]. Moreover, hydrogen fuel cells are a developing industry due to the inability to minimize size concerning energy potential when using hydrogen successfully. Nevertheless, the energy-to-mass ratio in the process is extremely high, and the energy-to-volume ratio is extremely low [91]. Hydrogen production from different feedstocks is presented in Table 4.

**Table 4.** Results for hydrogen production from different feedstock.

| Hydrogen Production        |                                                                  |                                       |                                                                                                                                                             |      |
|----------------------------|------------------------------------------------------------------|---------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Feed Stock                 | Operation Condition                                              | Yield                                 | Comments                                                                                                                                                    | Ref  |
| Food waste and brown water | pH: 5–5.5, TR: 133 days, T: 37 °C, Scale: two-phase CSTR         | 99.8 mL H <sub>2</sub> /g VS added    | The optimum hydraulic retention time (HRT) of the two-stage anaerobic digester system for hydrogen and methane production was determined.                   | [92] |
| Cassava wastewater         | pH: 5.5, TR: 40 days, T: 37 °C, Scale: two-phase continuous UASB | 39.83 L H <sub>2</sub> /kg VS removed | Hydrogen production from wastewater cassava starch production was maximized using two stages of anaerobic up-flow anaerobic sludge blanket (UASB) reactors. | [93] |
| Sugarcane juice            | pH: 4–5, TR: 213 days, T: 30 °C, Scale: Continuous EGBS          | 0.73 mol H <sub>2</sub> /mol hexose   | The influence of hydraulic retention time (HRT) on hydrogen production in three expanded granular sludge bed reactors (EGSBs) was evaluated.                | [94] |
| Food waste                 | pH: 5.5, TR: 18 days, T: 37 °C, Scale: Semi-continuous           | 14.66 mL/Vs added                     | The production and recovery performance of mixed VFAs and hydrogen using food waste through a submerged membrane was investigated.                          | [95] |

#### 2.4.3. Bio-Hythane

Hydrogen production can also be carried out through fermentative routes. Dark fermentation is considered to be the most efficient method [96]. Experimental yields of H<sub>2</sub> production failed to reach the theoretical yields due to problems such as high operating costs and the formation of inhibitory metabolites (e.g., mixed VFAs) [97]. AD is the best way to utilize mixed VFAs for CH<sub>4</sub> production in the form of biogas. This process also promotes H<sub>2</sub> production during the first three steps of digestion due to the coexistence of methanogens with H<sub>2</sub>-producing bacteria in the microbial consortium [98]. However, the conventional (one-step) AD process is structured to result in only CH<sub>4</sub> as a major part of the biogas, with only trace amounts of H<sub>2</sub>. By designing the AD as a two-stage process for the co-production of H<sub>2</sub> and CH<sub>4</sub> simultaneously instead of the one-step production, the thermal efficiency of the biogas can be improved. H<sub>2</sub> and CH<sub>4</sub> could complement each other and production in the form of “hythane” is gaining attention as a valuable fuel. Hythane is significantly advantageous over biogas in terms of its high-flammability range due to the presence of H<sub>2</sub>, as the flame speed is equal to seven times that of CH<sub>4</sub>. The term “hythane” is being replaced by “bio-hythane”, as organic waste is used as a substrate in the production process [99]. Bio-hythane is reported to be composed of between 5–30% hydrogen and 50–60% methane [100].

#### 2.4.4. Bio-Based Products

Digestate is the mixture of microbial biomass and undigested material produced in large quantities as a by-product of AD [101]. Digestate is usually separated mechanically into liquid (70%vol) and solid fractions (30%vol) to be stored separately for easy handling and transport. The liquid fraction contains a large part of N and K, while the solid fraction comprises many residual fibers and phosphorus [18]. Thus, digestate has been implemented as a soil improver or fertilizer in recent decades. Digestate application as a fertilizer represents an economic and environmental opportunity due to the generation of a value-added by-product [102]. In addition, this solid fraction represents an opportunity to substitute chemical fertilizers that have proven to be a source of significant environmental pollution [103]. For instance, Walsh et al. indicated that, unlike commercial fertilizers, liquid digestate can maintain or improve grassland crop yields and, at the same time, reduce nutrient losses to the environment [104]. Nevertheless, the use of digestate for land

application has also posed certain drawbacks. For example, because digestate must be stored, immediate implementation is not feasible; thus, the consequent loss of gases ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$ ) contributes to environmental issues [105]. Dragicevic et al. mention that digestate has a low nutrient retention capacity and groundwater could be contaminated due to possible leaching [106]. In this sense, different digestate valorization routes have been evaluated for obtaining products through various thermochemical technologies, such as gasification and pyrolysis, leading to the production of biofuels and biochar [107]. These alternatives promote a circular economy, close production cycles, and maximize economic and environmental benefits [108]. Table 5 presents the digestate composition under different feedstock sources for biogas generation.

**Table 5.** Digestate composition obtained from different feedstock sources [102].

| Parameter | Unit    | Grass | Organic Waste | Food Waste | Poultry Manure |
|-----------|---------|-------|---------------|------------|----------------|
| Ms        | %       | 8.12  | 14.05         | 3.83       | 7.8            |
| pH        | -       | 7.8   | 7.8           | 7.9        | 7.9            |
| N total   | kg/mg   | 5.56  | 6.64          | 6.29       | 6.7            |
| C total   | %wt     | 36.2  | 29.1          | 36.2       | 35.1           |
| C/N       | -       | 5.29  | 6.15          | 2.18       | 4.09           |
| P         | %wt     | 0.906 | 0.604         | 1.5        | 1.83           |
| K         | %wt     | 5.59  | 2.48          | 4.1        | 4.9            |
| S         | g/kg rm | 0.906 | 0.604         | 1.5        | 1.83           |
| Mg        | g/kg rm | 1.86  | 3.87          | 3.62       | 2.76           |
| Ca        | g/kg rm | 0.541 | 0.71          | 0.286      | 0.879          |
| Na        | g/kg rm | 0.592 | 8.26          | 50.3       | 3.83           |

rm: Raw material.

#### 2.4.5. Byproducts: Volatile Fatty Acids (VFAs)

Microbial processes have been categorized as possible routes to produce mixed VFAs through pure cultures, to obtain a specific fatty acid, or through mixed cultures by the AD process [109]. The production of mixed VFAs from microbial cultures allows for the utilization of renewable feedstocks, representing an advantage compared to conventional routes. In addition, mixed-VFAs production generates safer products for human health and offers high product selectivity. Consequently, mixed culture microbial processes present certain advantages compared to pure cultures in terms of utilization of several feedstocks (e.g., food waste, agricultural waste, sewage sludge). In addition, this process allows for energy savings as it can be conducted in non-sterile conditions [13]. AD technology is used in various countries for waste valorization in biogas production [110]. Several investigative approaches have been proposed to finalize the AD process at the acidogenic stage for mixed-VFAs production (termed acidogenic fermentation) [111]. Different reports suggest that mixed-VFAs production from AD has started to improve in terms of increasing efficiency, optimizing operating conditions, providing a renewable and sustainable source as a substrate, defining and evaluating microbial communities with the respective interactions, and new separation techniques [112]. Mixed-VFAs production processes from different feedstocks are presented in Table 6.

**Table 6.** Results for mixed-VFAs production from different feedstock.

| Mixed-VFAs Production        |                                                             |                     |           |           |         |                                                                                                                                                        |       |
|------------------------------|-------------------------------------------------------------|---------------------|-----------|-----------|---------|--------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Feed Stock                   | Operation Condition                                         | Yield (g VFAs/g VS) | VFAs %vol |           |         | Remarks                                                                                                                                                | Ref   |
|                              |                                                             |                     | Acetic    | Propionic | Butyric |                                                                                                                                                        |       |
| Organic solid waste          | pH: 10, TR: 10 days, T: 30 °C, Scale: Laboratory            | 0.83                | 70        | 7         | 13      | Seven organic waste streams were treated. Slaughterhouse wastewater produced the highest mixed VFAs yield.                                             | [113] |
| Food waste                   | pH: 6, TR: 20 days, T: 30 °C, Scale: Laboratory             | 0.91                | 70        | 5         | 17      | Mixed VFAs were significantly improved using anaerobic activated sludge to inoculate food waste.                                                       | [114] |
| Food waste                   | pH: 6, TR: 17 days, T: 30 °C, Scale: Laboratory             | 0.79                | 30        | 2         | 60      | The effects of redox potential (ORP) and inoculum on the production of mixed VFAs were evaluated.                                                      | [115] |
| Livestock and poultry waste  | pH: 5.5, TR: 4 days, T: 35 °C, Scale: Batch reactor         | 0.67                | -         | -         | -       | The effect of pretreatment and feed-to-microorganism ratios on the rapid generation of mixed VFAs was investigated.                                    | [112] |
| Waste activated sludge       | pH: 9, TR: 6 days, T: 55 °C, Scale: Semi-continuous reactor | 0.42                | -         | -         | -       | The sludge was subjected to a gradual increase in pH from 7 to 10. Maximum acidification was obtained at pH 8.9.                                       | [58]  |
| Municipal organic waste      | pH = 4.8–5.7, TR: 10 days, T: 55 °C, Scale: CSTR reactor    | 0.28                | 31–41     | 2–7       | 18–65   | Hydrogen production was evaluated under thermophilic acidogenic conditions. In addition, the best operating conditions for the process were evaluated. | [116] |
| Food waste                   | pH: 6, TR: 5 days, T: 35 °C, Scale: CSTR reactor            | 0.31                | 31        | 7         | 42      | Different operating conditions (pH, temperature, and OLR) were evaluated in producing mixed VFAs from food waste to achieve maximum yields.            | [117] |
| Food waste                   | pH: 6, TR: 17 days, T: 30 °C, Scale: Batch reactor          | 0.79                | 15        | 26        | 50      | Mixed VFAs were produced from three different substrates (glucose, peptone, and glycerol).                                                             | [118] |
| Starch industrial Wastewater | pH: 6, TR: 10 days, T: 25 °C, Scale: Batch reactor          | 0.78                | 40        | -         | 25      | The effect of varying the ratio of starch-rich wastewater to municipal wastewater on the production of mixed VFAs was studied.                         | [119] |
| Vinasses                     | pH: 5.5, TR: 10 days, T: 25 °C, Scale: Batch reactor        | 0.62                | 25        | -         | 54      | The potential of vinasse as a substrate for producing biohydrogen and mixed VFAs was evaluated.                                                        | [120] |

### 3. Volatile Fatty Acids Production

Pure VFA production is generated from conventional thermochemical processes (90%) [121]. Chemical synthesis has high production yields. Nevertheless, by using non-renewable sources as raw materials, this process incurs high environmental pollution. Alternative bio-based routes cover the remaining percentage. These routes have lower yields compared to conventional routes [122]. The wide industrial interest in pure VFAs is due to the various applications offered [123]. Moreover, the most often marketed pure VFAs are acetic, butyric, propionic, valeric and caproic acid.

#### 3.1. Acetic Acid

Acetic acid ( $\text{CH}_3\text{COOH}$ ) is the most widely used organic acid and one of the most commercially important pure VFAs. Acetic acid is a product with a wide range of applications in, for example, the pharmaceutical, food, and textile industries. Over 65% of production is directed to manufacture polymers derived from vinyl acetate or cellulose acetate [124]. On the other hand, the world demand for 2020 was estimated at 16.1 million tons [125]. The production of acetic acid can be carried out by different technologies. Traditionally, thermo-catalytic routes have been the predominant ones in the chemical industry, prevailing in methanol carbonylation, where methanol with excess carbon monoxide from synthesis gas is used [126]. Regarding biological production routes, several microbial strains have been investigated for acetic acid production, including *Acetobacter* *Thermoanaerobacter*, among others [127].

#### 3.2. Propionic Acid

Propionic acid ( $\text{CH}_3\text{CH}_2\text{C}_2\text{H}$ ) is a colorless water-soluble organic acid with a characteristic odor. The propionic acid market generated USD 1200 million in 2018 [128]. Propionic acid has a high commercial level and is used in various industries. This chemical is widely used to manufacture herbicides. In the food industry, this acid is used for emulsions or as a preservative because of the various bacteria growth-inhibition qualities [129]. Commercial production of propionic acid is mainly through chemical synthesis. Generally, the following three routes are used: (i) carboxylation of ethylene with carbon monoxide and water; (ii) ethylene hydroformylation/ethylene oxidation; and (iii) direct hydrocarbon oxidation. On the other hand, propionic acid biosynthesis is mainly carried out by using bacteria of the genus *Propionibacterium*. Several strains, such as *P. acidipropionici* and *P. freudenreichii*, produced propionate from hexoses and pentoses [130].

#### 3.3. Butyric Acid

Butyric acid ( $\text{C}_4\text{H}_8\text{O}_2$ ) is a colorless oily liquid with an unpleasant odor. This acid is naturally found esterified in animal fats and vegetable oils [131]. The global market for butyric acid derivatives is estimated to reach USD 170 million by 2026 [132]. Butyric acid and the derivatives have many applications in different industrial sectors (pharmaceutical, food, polymeric). Industrial production of butyric acid is mainly carried out by chemical synthesis during the oxidation of butyraldehyde obtained from propylene by oxo synthesis. This route is the most attractive from an economic point of view. Nevertheless, the food industry does not use chemically obtained butyric acid [129]. Thus, biological production is performed through fermentation using different microorganisms (e.g., *p. Butyrivibrio*, *Butyribacterium*, *Clostridium*, *Eubacterium*). *Clostridium* bacteria is the most used industrially due to the high productivity and the ability to use different substrates as carbon sources [133].

### 4. Mixed Volatile Fatty Acids by Anaerobic Digestion

#### 4.1. Upstream Process of Mixed Volatile Fatty Acids Production

The performance of the modified AD process to produce VFA can be improved. Pretreatments have proven an interesting approach to increase the mixed-VFAs production yield [134]. Pretreatment is generally performed when the feedstocks are difficult for

microorganisms to degrade (e.g., lignocellulosic wastes). Studies specifically focused on VFA production for this process are scarce. Table 7 presents reports on the pretreatment of different feedstocks to obtain better VFA production yields. The main pretreatments involve physical, chemical, physicochemical, and biological processes. The pretreatment type selection must address not only the performance of the process but also the economic feasibility of the process to be implemented and applied. Techno-economic analyses of biomass pretreatment systems applied to digestion processes often lack a basis for direct comparison due to different feedstock properties and system designs. Roger J et al. [135] evaluated various thermochemical pretreatment strategies (acid, alkaline, sulfite) techno-economically for anaerobic manure digestion. Moreover, three biogas utilization scenarios (electricity, biomethane, liquefied biomethane) were considered to determine the price at which each biogas byproduct using the technology becomes economically viable in a North American context. The techno-economic analysis revealed that pretreatment with moderate acid works best for larger facilities ( $\geq 5000$  animal units), while very alkaline pretreatment is preferred for smaller facilities. Rufino B et al. [136] evaluated the technical and economic feasibility of alkaline pretreatment (NaOH) to improve the AD of activated sludge. The economic analysis performed in this work showed that if the pretreatment was performed with an alkali dose of 0.08 g NaOH/g TS, only an increase in methane yield of 60% could compensate for the cost of the chemicals.

**Table 7.** Results of different pretreatment techniques for VFA production.

| Pretreatment     | Feedstock                            | Results                                           | Remarks                                                                                                        | Ref.  |
|------------------|--------------------------------------|---------------------------------------------------|----------------------------------------------------------------------------------------------------------------|-------|
| Chemical         | Alkaline                             | 12.5-fold increase in VFAs recovery               | NaOH was used to adjust the pH to 10                                                                           | [137] |
|                  | Acid                                 | 15.3-fold increase in VFAs recovery               | HCl was used to adjust the pH to 3                                                                             |       |
|                  | Nitrous acid                         | 3.7-fold increase in VFAs recovery                | Reduced fermentation times were achieved by improving hydrolysis.                                              | [138] |
|                  | Alkali                               | 4-fold increase in VFAs recovery                  | Pretreatments with three alkalis (NaHCO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> and NaOH) were applied. | [139] |
| Physical         | Heat treatment                       | VFAs recovery was increased 6.8-fold.             | It was determined that sludge pretreated at 100 °C for 60 min can achieve maximum hydrolyzation.               | [140] |
|                  | Heat treatment                       | 30.53% increase in VFAs production was achieved.  | The heat treatment was performed in an autoclave at a temperature of 121 °C for 30 min.                        | [141] |
|                  | Microwave                            | A 4.74% increase in VFAs production was achieved. | For microwave pretreatment 700 W; 170 C; 30 min were chosen                                                    |       |
| Physico-chemical | Thermal- alkaline                    | VFAs production increased by more than 60%.       | The raw material was exposed to alkaline treatment at pH 12 for 30 min using NaOH.                             | [141] |
|                  | Expansion/explosion of ammonia fiber | Achieved 21% increase in VFAs production          | An ammonia/raw material ratio of 1.5, a temperature of 93 °C, and a time of 15 min were used.                  | [142] |

#### 4.2. Downstream Process of Mixed Volatile Fatty Acids Production

One of the main challenges for using mixed VFAs from AD is the recovery process because mixed VFAs form an azeotropic mixture with H<sub>2</sub>O. A multi-phase enrichment and separation process is generally required to obtain marketable products from biomass transformation effluents [143]. Separation and recovery are even more difficult for individual VFAs, rather than mixed VFAs. Some studies have investigated these issues. Lopez-Garon and Straathof [144] have provided a detailed review of the recovery of individual carboxylic acids from pure culture fermentations. While the general processing steps are likely similar, the recovery of mixed VFAs is more complicated due to the mixture of acids that must be separated for sale as individual chemicals. Before choosing a separation process,

use of the mixed VFAs as a product should be considered, as this will influence downstream processing [127]. The recovery process should selectively focus on mixed VFAs over other fermentation broth components. Many methods of mixed VFAs recovery have been evaluated. Among these methods, liquid–liquid extraction, electrodialysis, nanofiltration, adsorption, and ion exchange have been analyzed. Table 8 presents some results reported in the literature. Pure VFA recovery should consider the abovementioned processes in the previous section. Few reports of the economic analysis of the recovery process of mixed VFAs obtained from AD have been found in the literature. The main difficulties reported in the literature are related to the range of VFAs produced and their separation routes. Bonk et al. [145] attempted to solve this problem by assuming a selling price for the VFAs, indicating the maximum allowable purification cost. Mixed VFAs were assumed to separate into their acids, creating numerous product streams. Considering organic waste as raw material, a maximum production cost of US\$14.96/m<sup>3</sup> of effluent was achieved. On the other hand, Fasahati [146] performed an economic evaluation of VFAs production by AD from algae and the separation of VFAs from the fermentative broth through different distillation columns. In addition, the economic variation of the process by integrating membrane distillation to increase the concentration of recovered VFAs was evaluated. This analysis was carried out with Aspen Plus v8.4 software. The selling price of VFA was determined to reach a break-even point after 10 years of plant operation of 384 USD/ton. These results were compared to the current price of acetic acid (1200–1500 USD/ton), thus showing the economic advantages of this process.

**Table 8.** Some reports on mixed VFAs separation techniques.

| Separation Technique        | Feedstock                                | Characteristics of the Separating Agent                      | Mixed VFAs Selectivity                                          | Ref   |
|-----------------------------|------------------------------------------|--------------------------------------------------------------|-----------------------------------------------------------------|-------|
| Absorption and ion exchange | Food waste                               | Amberlite IRA-67 and activated carbon were used as sorbents. | Predominant to recovery of butyric acid followed by acetic acid | [147] |
| Distillation                | Liquid effluent from palm oil production | Pilot scale distillation unit                                | Predominant to butyric acid recovery followed by acetic acid    | [148] |
| Electrodialysis             | Sucrose solution                         | Anionic and cation exchange membrane stack                   | Predominant to acetic acid recovery followed by butyric acid    | [149] |
| Liquid-liquid extraction    | Sugar solution                           | -                                                            | Predominant to butyric acid recovery followed by acetic acid    | [11]  |
|                             | Sewage sludge                            | trioctilamina in n-octanol                                   | Predominant to butyric acid recovery followed by acetic acid    | [150] |
| Membrane extraction         | Synthetic VFAs solution                  | Commercial membrane                                          | Predominant in the recovery of acetic acid                      | [143] |

#### 4.3. Mixed Volatile Fatty Acids Applications

VFAs generated from AD are characterized by being in the liquor interacting with each other. Due to the difficulty and limitations of the methods described above in separating the acids, several alternatives have been proposed for using the mixed VFAs as substrates to generate high-value products such as bioplastics and biofuels.

##### 4.3.1. Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHA) are biodegradable polyesters that can be produced from biological routes using renewable resources [151]. This plastic represents a promising alternative for the substitution of plastics derived from non-renewable resources. The

production of PHA has the limitation that its production costs are between 5 to 10 times higher compared to conventional technology [152]. PHA production by biological routes is conventionally performed by pure microbial cultures. The production yield of PHA is significant; however, it requires sterilization pretreatments, the selection of a specific substrate, and subsequent purification processes that raise production costs considerably [145]. In this sense, the production of PHA by residual organic sources represents a promising alternative. In recent years, mixed microbial cultures have been used to reduce the cost of PHA production. Several microorganisms, such as *Alcaligenes eutrophus*, *Bacillus megaterium*, and *Rhizobium*, among others, can consume VFAs as carbon sources to produce PHA [153]. Moreover, PHA production using organic wastes does not require sterility, making it much more attractive than pure microbial culture. Reis M et al. [154] noted that a 50% reduction in production cost can be achieved.

#### 4.3.2. Biodiesel

Biodiesel has emerged as an alternative to fossil fuel substitution. The limitation in the use of food crops for fuel production has been the main influencer in the search for other promising feedstocks [155]. Several studies have shown that waste-derived mixed VFAs can be converted into microbial lipids for biodiesel production [156]. Fei et al. [157] investigated the use of mixed VFAs for microbial lipid accumulation in *C. albidus* cultures and achieved a lipid content of up to 27.8% with a lipid yield in mixed VFAs of 0.167 g/g of *C. albidus* at acetic, propionic, and butyric levels. Park et al. [158] used rice straw residues in AD for mixed-VFAs production and subsequent conversion to major compounds for biodiesel production. Within the results, they identified that mixed VFAs derived from rice straw waste resulted in a yield of 0.43 g VFAs/g substrate and a 40% higher specific growth rate ( $0.305\text{ h}^{-1}$ ) than synthetic VFAs. VFAs as a carbon source resulted in a cetane number of 56–59, which is suitable for biodiesel production.

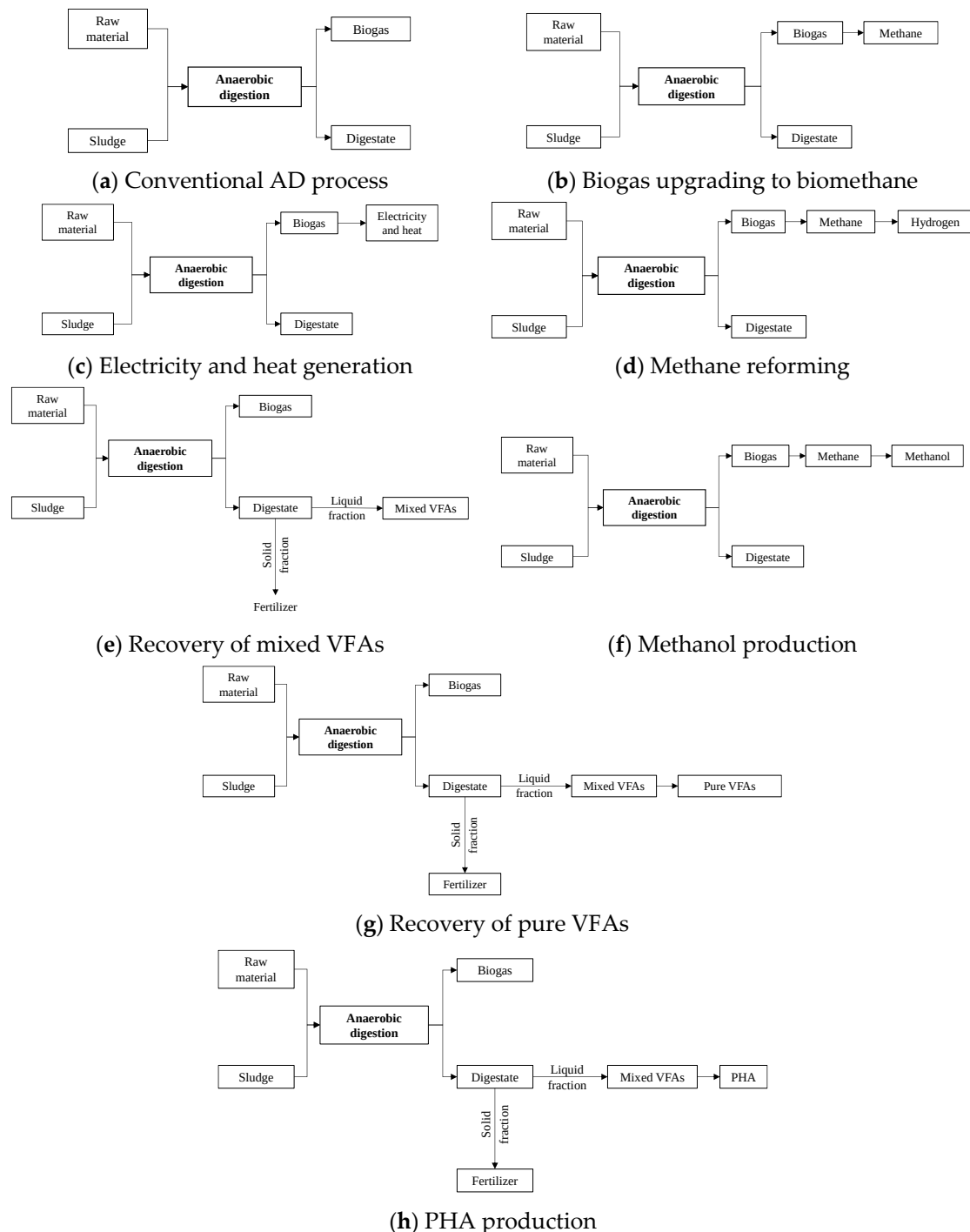
#### 4.3.3. Nutrient Removal

Due to the versatility of mixed VFAs produced from AD, other valorization alternatives have been proposed that are highly promising. For example, mixed VFAs can be used as an easily degradable and cost-effective carbon source for biological nutrient removal processes in wastewater treatment plants [159]. As reported by Shen et al. [160] mixed VFAs are only present in small amounts in wastewater, thus the addition of VFAs is required. Synthetic VFAs can be used as an additional carbon source, but represent additional costs; therefore, as an economical solution, mixed VFAs can be produced on site through sludge AD and then introduced into the treatment steps in the process. Simon, G. [161] mentions that the production of sufficient mixed VFAs from sewage sludge and their use for water treatment is more cost-effective than the conventional chemical flocculation process. From a 50:50 acetic and propionic acid ratio, phosphorus removal was achieved.

### 5. Mixed Volatile Fatty Acids and Anaerobic Digestion Potential in Biorefineries

The term ‘anaerobic biorefinery’ is a promising concept, where the anaerobic digester acts as the backbone for the transformation of raw materials into various high-value products or intermediates. The AD process has several associated benefits (e.g., reduction in organic wastes, reduction in the environmental burden of the current disposal of these wastes, valorization of these wastes, among others) [162]. Conventional AD already applies the biorefinery concept due to obtaining energy in the form of biogas and high-value products (digestate). However, emerging processes involving all the fractions obtained in integral transformation routes still need to be valorized or proposed. When the operating conditions of the process are kept in the optimal range, the microbial consortium (depending on the digestion route) may contain non-degraded compounds of interest (digestate). In subsequent processes, the digestate may contain valuable compounds that can be utilized. For example, when lignocellulosic materials are used as a substrate, the digestate may contain cellulosic fibers that can be transformed into sugars. These sugars

can then be precursors for the production of various products (bioenergy, organic acids, and biopolymers) [28]. Figure 5 present the schematic of an anaerobic biorefinery for producing bioenergy and bio-based products.



**Figure 5.** Several schemes of biorefineries based on the AD process.

There are several alternatives for using the digestion process as a valuable tool for generating a wide range of products, including: (i) AD modified to favor other metabolic pathways (e.g., acidogenic stage, acetogenic stage). This enables valuable compounds such as mixed VFAs to be obtained [36]. These are economically more attractive than biogas. Separation and purification techniques can be performed to generate pure VFAs. They can also be used as substrates to be implemented in other processes (e.g., PHA production); and

(ii) the generation of valuable products from conventionally generated AD products. The biogas generated can be implemented in reforming processes for  $H_2$  production.  $H_2$  has an energy potential 21 times higher than biogas. It can also be transformed into methanol, which facilitates its transport.

## 6. Case Study: Organic Kitchen Food Waste Valorization through Biorefinery Concept from Anaerobic Digestion

The case study involved experimental and simulation procedures. Biogas and mixed-VFAs production, using organic kitchen food waste (OKFW) as feedstock, was considered. The experimental procedures included (i) feedstock characterization and (ii) biogas and mixed-VFAs production considering different scenarios. The best experimental results were used as input data for the simulation. The simulation was performed using Aspen Plus software, contemplating different scenarios. Mass and energy balances were obtained from the simulation. Finally, economic metrics were determined to estimate the economic feasibility of the scenarios.

### 6.1. Experimental Procedure

A compositional model described by Ortiz et al. was used [163]. The compositional model contemplates a mathematical expression involving seven food groups (e.g., dairy products, meat products, fruits, and vegetables). Based on databases reported by governmental entities on consumption statistics in the Colombian context, the most representative foods were defined according to the basic family food basket. Cassava (16.85%), onion (11.14%), tomato (9.93%), potato peel (8.42%), and rice (9%) were the most representative foods. The composition of OKFW was performed manually in the laboratory according to the composition model.

OKFW characterization was estimated to analyze fats, extractives, cellulose, hemicellulose, lignin, ash, proximate, and solids. Fats were quantified using n-hexane [164]. Extractives were measured by applying the Technical Report NREL/TP-510-42619 [165]. Holocellulose was determined by the chlorination method [166]. Insoluble lignin was measured as Klason lignin according to the Technical Report NREL/TP-510-42618 [167]. For the proximate analysis, volatile matter was determined following the ASTM D7582-15 standard method [168]. Fixed carbon content was measured by difference. Total and volatile solids were estimated following the ASTM E1756-08 standard method [169]. All characterizations were performed on the dried raw materials in triplicate.

Three different feedstock conditions were considered for biogas production. Scenario 1 (OKFW\_Pretreated\_B) contemplated biogas production with thermally pretreated feedstock. The pretreatment was performed with liquid hot water (LHW) at 80 °C for two hours with constant agitation and a solid: liquid ratio of 1:10. Scenario 2 (OKFW\_Wet\_B) contemplated using fresh raw material (moisture content 79 %wt). Scenario 3 (OKFW\_Dry\_B) considered the use of dry OKFW. The homogenized sample was dried at 40 °C for 24 h for this scenario. Then, the sample was crushed with a knife mill until a particle diameter of 0.45 mm was obtained.

Finally, the previously mentioned raw material conditions were considered for the mixed-VFAs production in Scenario 4 (OKFW\_Pretreated\_V), Scenario 5 (OKFW\_Wet\_V) and Scenario 6 (OKFW\_Dry\_V), respectively. Moreover, for both processes, the efficiency of the digestion process was ensured by adding a micronutrient solution and a macronutrient solution, according to Angelidaki, I. et al. [170].

Biogas production was developed according to the VDI 4630 standard method [171]. A volatile solids ratio of feedstock to inoculum of 0.4 was used. The temperature was 37 °C, and the initial pH was 7. The digestion time was 26 days. In addition, to ensure an oxygen-free medium, nitrogen injection was performed. Sludge from a coffee-processing plant anaerobic reactor was used as inoculum. The sludge had a total and volatile solids content of 6.7% and 6.1%, respectively. Biogas production was determined by volumetric

displacement, and its composition was measured with a gas analyzer (Gasboard-3100P, Cubic, Taiwan, China).

VFAs production was performed according to Iglesias R [172]. A volatile solids ratio of feedstock to inoculum of 1 was used. The temperature was 37 °C with an initial pH of 5.5. Digestion time was 10 days [173]. In addition, to ensure an oxygen-free medium, a nitrogen injection was performed. VFAs production was determined from a colorimetric method described by Montgomery [174]. The absorbance was determined at a wavelength of 500 nm in a spectrophotometer (UV/Visible Model 6405, Jenway, Felsted, UK). Acetic acid at different concentrations was used to perform the standard curve.

### 6.2. Simulation Procedure and Process Description

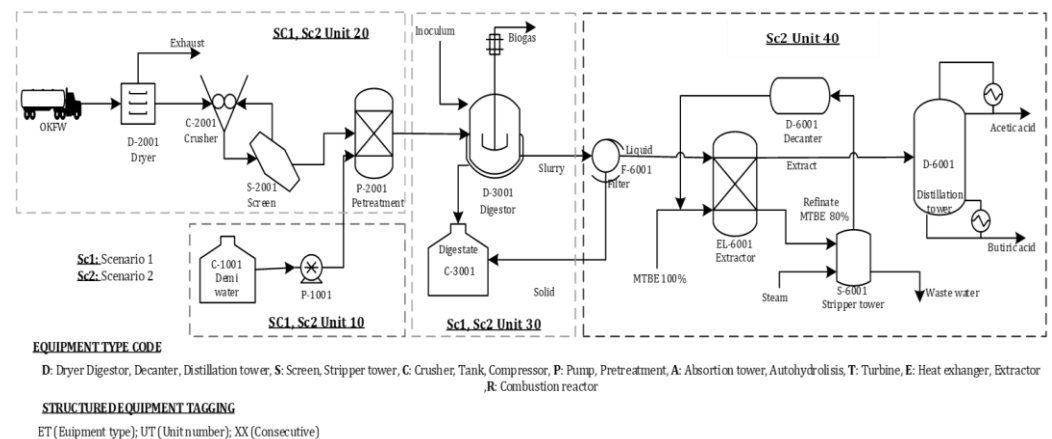
The simulation was performed with Aspen Plus software (v.9) using an OKFW mass flow of 2.07 tons/day according to OKFW generated in Sincelejo, Sucre in Colombia. Biogas production was simulated using the non-random two-liquid activity (NRTL) model and the Peng–Robinson equation of state to describe liquid and vapor phases [175]. In addition, the non-random two-liquid thermodynamic/activity model (NRTL-HOC) was selected for the simulation of VFAs production because it is suggested for processes involving carboxylic acids where separation processes from distillation are considered. The method uses the Hayden–O’Connell equation of state as the vapor phase model [146]. The best experimental results (mass balances) were taken as input data for the simulation to biogas and VFAs production.

The first three units (Unit 10, Unit 20, and Unit 30) are presented in the two proposed scenarios (see Figure 6). Equipment was defined according to the type of operating unit and application using an alphabetical system. The Units were identified using a numerical system for tagging the equipment and simplifying the logical categorization of the equipment. Unit 10 represented the storage area for the inputs required in the process. Unit 20 contemplated the conditioning of the OKFW. In this unit, OKFW were dried at 50 °C to a moisture content of 10% on a dry basis. Grinding was performed with a knife mill to a 1–2 cm mm particle size. Then OKFW was pretreated with LHW using a solid: liquid ratio of 10, the temperature of 80 °C at 1 bar, as reported by Yangyang Li et al. [176]. Unit 30 involved the AD. The operating conditions differed depending on the product (amount of sludge added and operating time). The temperature and pressure were 37 °C and 1 bar, respectively. Scenario 1 contemplated conventional anaerobic digestion (i.e., for biogas, solid and liquid fertilizers production). An inoculum: substrate volatile solids ratio of 0.4 was considered. Scenario 2 (Unit 40) comprised the AD modified to promote the production of mixed VFAs and liquid and solid fertilizer. An inoculum substrate ratio of 1 was used. Recovery of the mixed VFAs from the liquor was performed by liquid–liquid extraction (using methyl tert-butyl ether-MTBE). Then, purification was carried out by distillation [146]. For the simulation, the mixed VFAs described by Jianguo et al. [117] were considered (acetic acid 31% vol and butyric acid 41% v/v).

### 6.3. Techno-Economic Assessment

The technical assessment of the proposed scenarios was determined with mass and energy indicators. The simulation tool Aspen Energy Analyzer v.9.0 was used. The mass indicators evaluated were the process mass intensity index (PMI), which describes the relationship between the total raw material input flow and the total product output flow, and the product yield, which relates to the output product and the raw material flow. The production cost of the proposed scenarios included estimates for raw materials, utilities, and financing costs. The economic analysis was performed on a gross revenue basis. In addition, associated costs during the construction phase (e.g., equipment, instrumentation, labor costs, pipe supports, among others) were considered. Amortization of capital expenditures was calculated using the straight-line depreciation method. Annual operating costs were calculated based on industrial services and operating expenses. Capital expenditures were estimated using the Aspen Capital Cost Estimator (ACCE). The cost estimate was

developed assuming industrial costs in the second quarter of 2022. This analysis is a process in which new units are added downstream of anaerobic digestion to produce new integrated products. Therefore, specific parameters related to Colombian conditions in an existing facility, such as utility costs, income tax rate, and labor wages, among others, were incorporated to build the financial model and investment analysis. An annual interest rate of 17% and an income tax of 25% were considered. In addition, hours of work at 8000 h per year and three daily shifts were set [177]. Finally, the feasibility of the process required an evaluation of several factors. Thus, economic feasibility was analyzed through net present value (NPV) and payback period (PBP) metrics. Table 9 shows the costs and prices considered for the economic analysis.



**Figure 6.** Process flow diagram of biogas (Sc1) and mixed-VFAs (Sc2) production process.

**Table 9.** Costs and prices involved in the economic analysis.

| Item                   | Units              | Value  | Ref   |
|------------------------|--------------------|--------|-------|
| Utilities cost         |                    |        |       |
| Low-pressure steam     | USD/ton            | 1.57   | [175] |
| Electricity            | USD/kWh            | 0.022  | [175] |
| Labor cost             |                    |        |       |
| Operators wage *       | USD/month          | 232.15 | [178] |
| Supervisor wage **     | USD/month          | 464.29 | [178] |
| Chemical reagents cost |                    |        |       |
| Water                  | USD/m <sup>3</sup> | 0.32   | [175] |
| MTBE                   | USD/kg             | 1.10   | [146] |
| Product price          |                    |        |       |
| Acetic acid            | USD/kg             | 0.45   | [179] |
| Butyric acid           | USD/kg             | 1.30   | [179] |
| Solid digestate        | USD/ton            | 7.36   | [180] |
| Liquid digestate       | USD/ton            | 4.16   | [180] |
| Biogas                 | USD/m <sup>3</sup> | 0.79   | [181] |

\* Minimum wage 2022. Non-skilled person.; \*\* High-skilled person.

## 7. Results and Analysis

### 7.1. Raw Material Characterization

OKFW characterization and several results reported in the literature are presented in Table 10. The cultural and socioeconomic context strongly influences the OKFW composition. However, the results presented in this work are similar to those reported in the

literature. Furthermore, the characterization of OKFWs demonstrated their potential to be implemented in AD processes due to their high carbohydrate content (cellulose, hemicellulose). The OKFW exhibited fixed carbon, volatile matter, and ash contents of 16.16%, 77.8%, and 6.04%, respectively. In addition, it presented a lower heating value (LHV) of 15.26 MJ/kg. These results are similar to those reported in the literature [182].

**Table 10.** Costs and prices involved in the economic analysis.

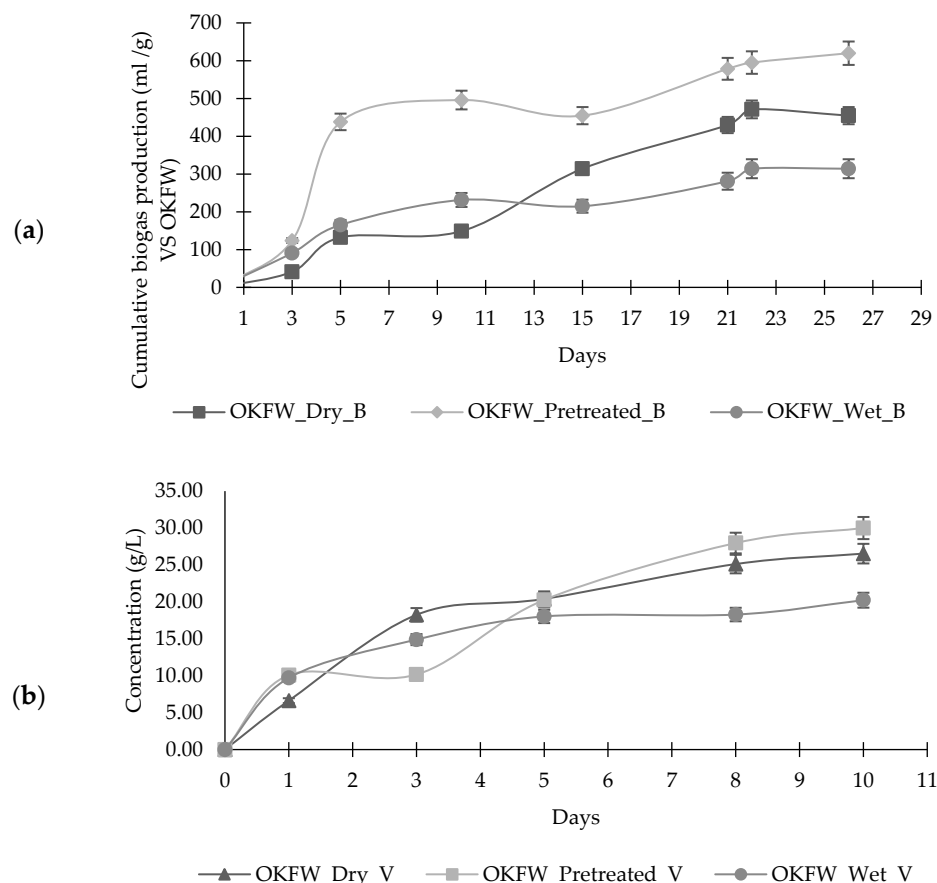
| Chemical Characterization | Cellulose | Hemicellulose | Lignin | Extractives | Ash  | Fats | Ref.      |
|---------------------------|-----------|---------------|--------|-------------|------|------|-----------|
| OKFW                      | 28.56     | 7.42          | 19.84  | 30.3        | 4.68 | 9.19 | This work |
| Dinner shop food waste    |           | 102.6         |        | N.R         | 1.25 | 3.1  | [183]     |
| Food waste (restaurant)   |           | 52.2          |        | N.R         | 5.51 | 16.2 | [184]     |

N.R. not reported.

## 7.2. Biogas and Mixed-VFAs Production

Figure 7a shows the cumulative biogas production for the three proposed scenarios during 26 days of digestion. The total biogas productivity was 395, 231, and 198 mL for OKFW\_Pretreated\_B, OKFW\_Wet\_B, and OKFW\_Dry\_B, respectively. Low biogas volumes were recorded from day 21 of digestion for all three scenarios, indicating that most of the feedstock was digested. It was observed that the LHW pretreatment was effective for the highest biogas production. This can be explained by the fact that many free sugars or low-molecular-weight molecules in the medium are easily degradable by microorganisms [185]. The CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S content was 53.4%, 40.8%, and 50 ppm, respectively. Gandhi P et al. showed that with LHW pretreatment of food waste, biogas production increased by 40% [186]. On the other hand, OKFW\_Dry\_B presented the lowest biogas production yield. This demonstrated that the moisture content present in the feedstock directly affects substrate consumption. When the moisture content increased from 9.8% to 79%, biogas production increased by 23.59%. This can be attributed to the dilution of the mixed VFAs generated in the acidogenic stage. The water content favored the decreased inhibition of VFAs in the methanogenic stage. Similar results have been reported by Agnihotri S. et al. [121]. They evaluated the effect of moisture content, ranging from 97 to 89%, on the anaerobic digestion of sludge and showed that methane decreased from 330 to 280 mL/g VS.

Figure 7b presents the mixed-VFAs production for the three proposed scenarios during ten days of digestion. The operating conditions used in the digestion favored the growth of acidogenic microorganisms and, consequently, the production of mixed VFAs [77]. Mixed-VFAs production obtained maximum concentrations of 31, 26.53, and 20.23 g VFA/L in OKFW\_Pretreated\_V, OKFW\_Wet\_V, and OKFW\_Dry\_V, respectively. After day 5, the pretreated feedstock presented higher mixed-VFA production. This indicates pretreatment favored greater substrate accessibility for acidogenic microorganisms (monomers and oligomers). However, the remaining scenarios recorded lower amounts of VFAs, indicating that most of the substrate was consumed and probably initiated the growth of methanogenic microorganisms [187]. Similar VFAs concentrations have been reported in the literature. For example, Nuo Liu [188] obtained a maximum VFA concentration of 26.16 g VFA/L from food waste over five days. Liang W et al. [137] obtained a production of 56.7 g VFA/L over seven days using activated sludge. Moreover, the results also showed that pretreatment with acid and alkali improved VFAs production by 12.5 times. Regarding the initial moisture content of the feedstock, compared to biogas production, dry feedstock favors VFAs production. The low moisture content allowed a higher concentration of acid. This caused inhibition of methanogenic microorganisms.



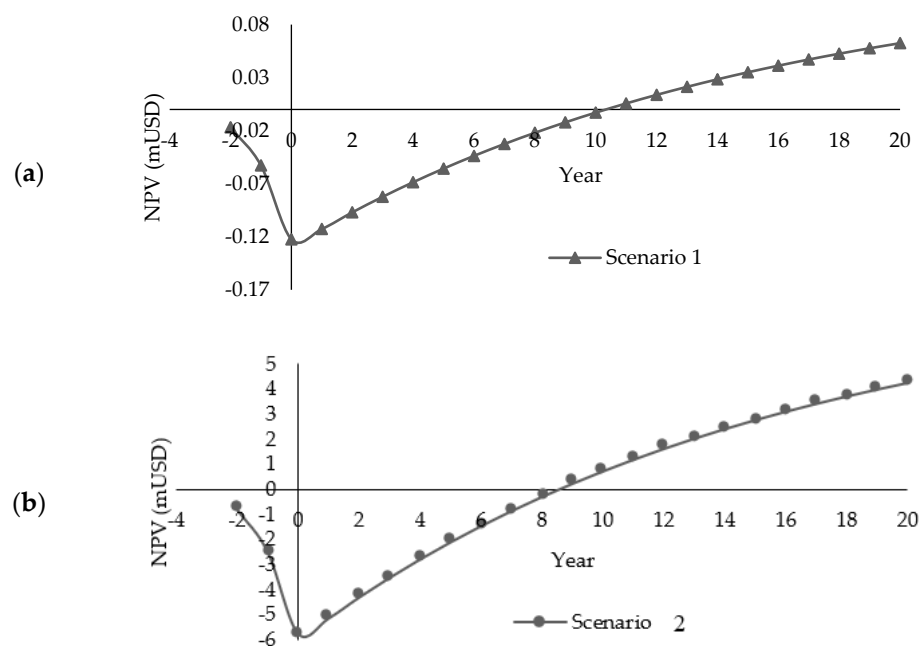
**Figure 7.** (a) Biogas; and (b) mixed-VFAs production for the proposed scenarios.

### 7.3. Techno-Economic Assessment

The best experimental results for biogas and mixed-VFAs production (OKFW\_Pretreated\_B and OKFW\_Pretreated\_V) were used as input data for the proposed scenarios for the simulations. The mass and energy indicators were determined from the mass and energy balances of the proposed scenarios. The first indicator evaluated was product yield. For scenario 1, a biogas production yield of 0.528 m<sup>3</sup> biogas/kg OKFW (0.571 kg biogas/kg OKFW) was obtained with a CH<sub>4</sub> content of 53.4%. In scenario 2, acetic acid and butyric acid production yield were 0.081 and 0.102 kg acid/kg OKFW, respectively. The yield values can be explained by considering the conversion pathways of each product. Only a percentage of the substrate is digested by the microorganisms. Another important factor contributing to the yield is product recovery from the fermentation broth. For example, the LLE unit, using MTBE as a solvent, achieves a 90% recovery of VFAs. The remaining 10% is lost in the wastewater. The process mass intensity index (PMI) is the mass of raw material required to produce 1 kg of product [189]. Scenario 1 presented a PMI index of 4.69. Scenario 3 presented an index of 7.41. These values were estimated to avoid process-water consumption in both processes, as indicated by Tobiszewski et al. [190]. To consider high efficiency, the PMI index should be 1. The results suggest that scenario 3 involves using more inputs (i.e., MTBE).

Considering operational expenses (OpEx), i.e., cost of raw materials, utilities, maintenance, labor, and capital depreciation for scenarios 1, the most significant costs were related to utilities and raw materials. The stage with the greatest contribution to the cost of utilities was the pretreatment stage. In the process, the utility costs did not increase because this process was carried out at 20 °C. For scenario 2, the feedstock costs were the most significant. This was due to the use of MTBE in the liquor VFAs extraction stage. As for capital expenditures (CapEx), the values for scenarios 1 and 2 were contrasted. Scenario 2 presented an increase of more than 60% in CapEx compared to scenario 1 due to the additional processing units. This has been observed by several authors who have

evaluated different VFAs recovery techniques (adsorption, membrane technology, solvent extraction) [191]. The level of VFAs production (butyric acid and acetic acid) and the high selling price compared to biogas production amortized the complexity of the process and made the process more attractive. Figure 8 shows the NPV over the project's life for the proposed scenarios. The NPV analysis calculates the economic benefits using cash flow balances. Two proposed scenarios demonstrated economic profitability due to the positive trend of NPV at a flow rate of 2.07 tons/day of raw material. A reduction of 17% of the PBP value was obtained compared to scenarios 1 and 2, respectively.



**Figure 8.** VPN of the project lifetime of the proposed scenarios: (a) scenario 1; and (b) scenario 2.

## 8. Conclusions

AD is a widely used technology for the degradation of organic matter and the generation of renewable energy. This technology plays an essential role in the organic waste conversion process. AD is characterized by not requiring strict conditions and can be applied to a wide range of raw materials. The operating conditions are designed to promote biogas production (i.e., the methanogenic phase). However, other metabolic pathways are promoted by variations in the operating conditions of the process. This promotes the production of compounds of high commercial interest such as mixed VFAs. Based on the analysis of the different AD routes performed in this study, it was demonstrated that this technology involves the biorefinery concept. Not only can energy be obtained in the form of biogas, but also high value-added products (mixed VFAs, solid and liquid digestate). AD in biorefineries is an essential component of biomass conversion, providing renewable energy in the form of biogas and useful chemicals or fertilizers from organic materials. AD contributes to reducing organic waste and greenhouse gas emissions, thereby becoming an important technology from an environmental and economic perspective. In fact, the technical and economic potential of AD for OKFW transformation towards energy vectors and high-value products in a Colombian context was demonstrated. VFAs have limitations in the market. There is no need for the high consumption of these acids to compete with biofuels, i.e., with biogas consumption. Energy is a necessary resource for all production processes. AD by-products applying the biorefinery concept (production of mixed VFAs, hydrogen, bio-hythane) have not been produced commercially until now. Moreover, they are still strongly dependent on fossil resources. However, their potential applications, as well as the market size, price, and producing companies are worth discussing. This is especially important due to the rapid depletion of fossil fuels and related

carbon footprint issues, which is leading to a shift from products based on conventional processes to the more environmentally friendly bio-based products created with an anaerobic biorefinery approach.

**Author Contributions:** T.A.-P.: Investigation, Methodology, Analysis, Writing—original draft, Edition, M.O.-S.: Investigation, Methodology, Simulation, Analysis, Writing—original draft, C.A.C.A.: Funding acquisition, Conceptualization, Supervision, Writing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This paper is the result of the research work developed through the research project “Aprovechamiento y valorización sostenible de residuos sólidos orgánicos y su posible aplicación en biorrefinerías y tecnologías de residuos a energía en el departamento de Sucre” code BPIN 2020000100189.

**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

**Conflicts of 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.

### Abbreviations

AD: Anaerobic digestion; VFAs: Volatile Fatty Acids, VC: Value Chain; MSW: Municipal solid waste; TR: Retention time, VS: Volatile solid; CSTR: Continuous Stirred Tank Reactor, UASB: Up flow anaerobic reactor, GHG: Greenhouse gas emissions, LHV: Low heating value; N.R: Not report; TS: Total solid; OKFW: Organic kitchen food waste; PHA: Polyhydroxyalkanoates; TMR: Representative market rate; NPV: Net present value, PBP: Payback period.

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