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Chapter

From Food Waste to Volatile Fatty Acids towards a Circular Economy

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Abstract

The food industrial sector generates large amounts of waste, which are often used for animal feed, for agriculture or landfilled. However, these wastes have a very reach composition in carbon and other compounds, which make them very attractive for valorization through biotechnological processes. Added value compounds, such as volatile fatty acids (VFAs), can be produced by anaerobic fermentation using pure cultures or mixed microbial cultures and food waste as carbon source. Research on valuable applications for VFAs, such as polyhydroxyalkanoates, bioenergy or biological nutrient removal, towards a circular economy is emerging. This enhances the sustainability and the economic value of food waste. This chapter reviews the various types of food waste used for VFAs production using mixed microbial cultures, the anaerobic processes, involved and the main applications for the produced VFAs. The main parameters affecting VFAs production are also discussed.

Keywords: acidogenic fermentation, volatile fatty acids, food waste, mixed microbial cultures, process parameters, applications

1. Introduction

The increase of industrialization and world population is leading to a huge generation of organic wastes, causing serious environmental problems if disposed without an adequate treatment [1, 2]. The conventional waste treatment is mainly focused on environmental regulations, neglecting the resource recovery from wastes streams, which is one of the environmental sustainability goals [2, 3]. The resource recovery allows the waste treatment and, simultaneously, the generation of added-value products, following the circular economy strategy. The conversion of food waste (FW) into valuable products, that can be used in daily activities, have been gaining more attention due to their potential and market opportunities [4].

One of the most common technology for waste treatment is the anaerobic digestion process (composed by four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis), where the organic matter is converted into valuable resources, as methane or volatile fatty acids (VFAs) (**Figure 1**). Although biogas is generally the final product of anaerobic digestion process, the production of VFAs from FW has gained a great attention due to their high market value, as well as due to their storage and transportation be easier and safer [5]. Furthermore, the production of VFA from FW allow the replacement of the traditional production from non-renewable petrochemical sources, contributing to the circular economy and environmental sustainability [3].

VFAs are linear short-chain fatty acids comprising two (acetic acid) to six (caproic acid) carbon atoms which can be distilled at atmospheric pressure [2].
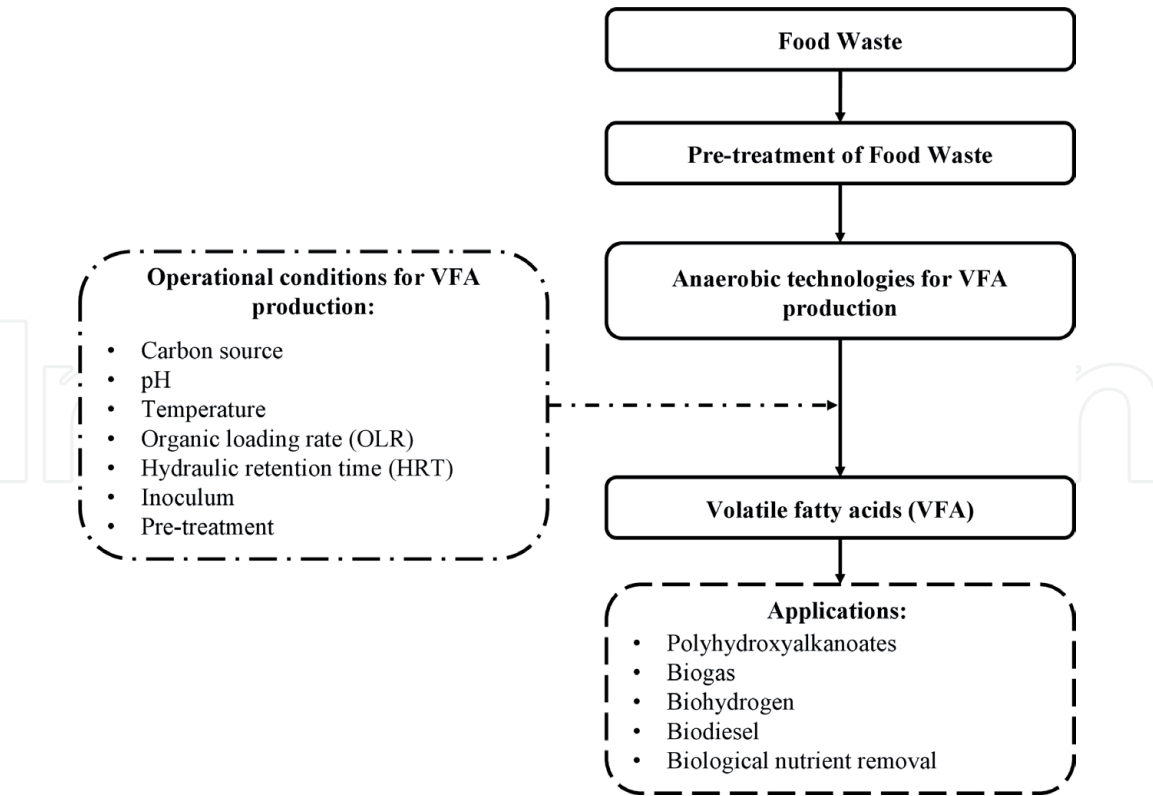
Figure 1.
Production of VFAs using FW as substrate: General process and applications overview. Adapted from lee et al. [2].

Actually, the production of VFAs is mainly accomplished by chemical routes through the oxidation or carboxylation of chemical precursors deriving from petroleum processing [6]. However, VFAs can also be biologically produced, using pure or mixed microbial cultures, in a single-stage anaerobic process. The use of mixed microbial cultures is emerging, as a broad spectrum of substrates can be used and sterile conditions are not required, lowering the production costs [7].

During the last years, several efforts have been done to improve the production of VFAs from FW through the assessment of different types of FW and optimization of operational conditions. Besides the type of FW used, operating parameters, such as pH, temperature, hydraulic retention time (HRT), inoculum, and organic loading rate (OLR) can affect the VFA production, composition and yield (**Figure 1**) [2, 3, 6]. VFAs have a broad spectrum of applications such as polyhydroxyalkanoates (PHAs), bioenergy (biogas, biohydrogen), biological nutrient removal, as well as in chemical industry as precursors in organic chemistry [2, 6]. Nowadays, it is known that by controlling the process it is possible to manipulate the VFA composition, which is an important factor considering the application of the VFA stream. For example, the manipulation of the VFA profile of the stream will allow to produce PHAs with different compositions and, consequently, with different applications (e.g. packaging, construction materials, medical applications, etc.) [8]. This chapter reviews sustainable processes for FW valorization through VFA production, which can minimize further environmental degradation and promote the evolution to a sustainable society, towards a circular economy.

2. Food waste

FW can be defined as "the final product of food chain that was not recycled or used for other purposes" [9] and corresponds to one third of the total food

production for human consumption [10]. FW is one of the most produced waste and it is estimated to increase by 44% until 2025 due to, both, economy and population growth [10, 11]. This high increase in FW production have led to the need to develop appropriate treatment technologies [7]. Landfill, composting, incineration and animal feed are the conventional methods for FW disposal/treatment, which present several environmental concerns, such as air, soil and groundwater contamination, greenhouse gas emissions, odor production, leaching and disease propagation (in case of animal feed) [9, 10, 12]. As such, anaerobic digestion has been widely used as an eco-friendly, sustainable and low-cost alternative technology, that allows to treat the waste and valorize them by the recovery of added-value products, such as methane, hydrogen or VFAs [7, 10].

FW composition depends on the habits and economical level of the region and the climate, showing different characteristics, such as pH, solid content, and carbon to nitrogen ratio (C/N) [5, 10]. Notwithstanding, easy biodegradability, nutrients availability and moisture content are similar features worldwide [5]. FW is rich in carbohydrates (hemicellulose, cellulose, starch, and sugar like sucrose, fructose, and glucose), proteins, lipids and inorganic compounds [11, 12]. The sugar content varies between 35 and 60%, while proteins and lipids vary between 15–25% and 13–30%, respectively [10, 12]. Due to the high nitrogen content of proteins, FW presents a low C/N ratio comparing with other substrates. Moreover, FW have high content of other elements, as phosphorus, sodium, potassium, calcium or magnesium, and low content of trace elements, as iron, selenium, nickel or molybdenum [10]. All these features make the FW an interesting renewable source for VFA production. Different types of FW, such as solid waste of cafeteria [13, 14], tuna waste [15], fruit pulp waste [1, 16], cheese whey [8, 17], sugar cane molasses [17], corn stalk [18], potato peel waste [19], FW rich in proteins [20], brewers' spent grain [21], mixture of different fractions of FW [22], FW from canteen [23, 24], and vegetable wastes [25] have been used as feedstock in biological processes using mixed microbial cultures. Furthermore, FW can be also mixed with other wastes, like as waste activated sludge [26] and sewage sludge [27] to improve the biological process performance.

3. Production of volatile fatty acids (VFAs)

The conversion of the organic content of waste into VFAs requires an acidogenic fermentation (AF). While soluble organics can be directly fermented into organic acids and other fermentation products, such alcohols and hydrogen, insoluble compounds need to be hydrolyzed prior to acidification, limiting the rate of VFA production [28, 29]. As such, the production of VFAs involves two steps: (1) hydrolysis, and (2) acidogenesis, commonly occurring in a single anaerobic reactor (**Figure 2**) [2]. In the hydrolysis step, enzymes excreted by hydrolytic microorganisms (e.g. *Clostridium* sp., *Bacillus* sp., *Bifidobacterium* sp.) brake down complex organics (such as proteins, cellulose, lignin, and lipids) into simpler soluble monomers (such as amino acids, simple sugars, glycerol, and fatty acids), which lead to an increase in the soluble chemical oxygen demand (sCOD). Then, these monomers are mainly converted into VFAs (such as acetic, propionic, butyric, and valeric acids) by fermentative bacteria (e.g. *Acetovibrio cellulolytic*, *Butyrivibrio* sp., *Selenomonas* sp.) in the acidogenic fermentation step (acidogenesis) [2, 30–32].

The production of VFAs from acidogenic fermentation of FW involves a series of chemical reactions, where different metabolic pathways co-exist within the anaerobic digester. These pathways play a crucial role in the system performance and consequently in the FW conversion efficiency. Pyruvate is the primary intermediate
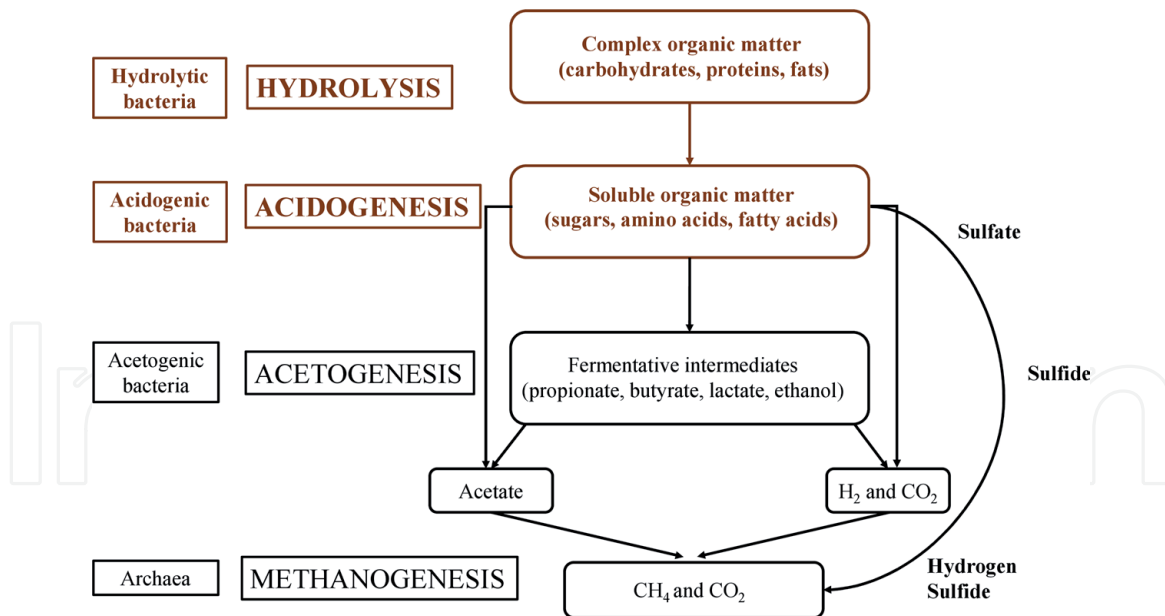
Figure 2.
Overall anaerobic digestion process schematic representation.

and can be converted into a wide range of products, such as VFAs, alcohols, hydrogen, and carbon dioxide. The type of substrate used, the environmental conditions and the microorganisms present in the reactor affects the proportions of pyruvate in each metabolic pathway and consequently the distribution of VFAs produced [5]. The acidogenic metabolic pathways can be classified in: acetate-ethanol type; propionate-type; butyrate-type; mixed-acid and lactate-type, depending on the main products produced during the acidogenic fermentation.

Acetate can be produced from acetyl-CoA pathway or from the syntrophic oxidation of ethanol or longer chain fatty acids. Ethanol can be produced from pyruvate in two or three steps, depending on the type of bacteria, and with acetyl-CoA and acetaldehyde as intermediates [5]. Propionate is produced by two distinct pathways: (1) pyruvate is reduced by the catalyzation of lactate dehydrogenase and then lactate is reduced to propionate through the propionate dehydrogenase; (2) propionate is produced by acidogenic bacteria (e.g., Corynebacteria, Propionibacterium and Bifidobacterium) via transcarboxylase cycle. Butyrate production from pyruvate comprises: (1) pyruvate conversion into acetyl-CoA by pyruvate dehydrogenase; (2) acetyl-CoA is converted into to butyryl-CoA with acetoacetyl-CoA, 3-hydroxybutyryl-CoA and crotonyl-CoA as intermediates sequentially by the catalysis of thiolase, 3- hydroxybutyryl-CoA dehydrogenase and butyryl-CoA dehydrogenase; (3) butyryl-CoA is converted into butyrate by phosphotransbutyrylase and butyrate-kinase enzymes or by the butyryl-CoA: acetate CoA-transferase [5]. For the lactate production, pyruvate is converted to lactate through lactate dehydrogenase and can be divide into two fermentation types: homolactate fermentation (one mole of glucose is converted into two moles of lactic acid) and heterolactate (lactic acid is produced with carbon dioxide and ethanol). In mixed fermentation, an equal amount of each acid is produced with a possible formation of carbon dioxide and hydrogen. This type of fermentation is common in FW fermentation with acetate and butyrate the main metabolites produced. Acetate can be also produced by homoacetogens, which are obligate anaerobes that can use hydrogen to reduce carbon dioxide to acetate. In autotrophic process, the homoacetogens consumed hydrogen and carbon dioxide producing acetate by Wood-Ljungdahl pathway [5].

Since acidogenesis is the second step of the anaerobic digestion of organic compounds into biogas (methane and carbon dioxide), high pH (above 8) or low pH (bellow 6), low temperature and/or low HRT are usually used to prevent methanogenic activity (**Figure 2**). Moreover, the operating parameters of the acidogenic fermentation, such as HRT, sludge retention time (SRT), organic loading rate (OLR), pH, temperature, and reactor configuration, must be optimized aiming at VFAs production yield maximization and at controlling the composition of the synthesized VFAs.

VFAs production from FW using mixed microbial cultures is mostly based on the use of suspended biomass. Thus, continuous stirred tank reactors (CSTR), stirred tank reactors (STR) and immersed membrane bioreactors are being applied for that purpose [1, 15, 21, 22, 33, 34]. Those reactors are usually operated in a continuous mode. However, for FW needing high retention times to be converted into VFAs, they are often converted into batch and semi-continuous (fed-batch) reactors [15, 19, 21, 33–38].

4. Effect of process parameters in VFAs production

The production of VFAs through FW fermentation using mixed microbial cultures, as well as the VFA composition and yield, are influenced by numerous factors, such as carbon source, pH, temperature, HRT, inoculum, and OLR [2, 3, 6, 7].

4.1 Carbon source

The type of carbon source, namely the complexity and composition, affects the acidification degree, since this depends on the readily fermentable organic fraction, and consequently, influences the production of VFAs [3, 25]. The content of carbohydrates, lipids and proteins influences the production of VFAs, since each fraction present different biodegradability and hydrolysis efficiency [6]. Moreover, the type of acids produced depends on the waste composition. The fermentation of carbohydrates, proteins and lipids form directly acetic, propionic, and butyric acids, while valeric and iso-valeric acids are related to the fermentation of proteins [15]. Lipids are the fraction more resistant to the biodegradation, being less suitable for AF than the other FW fractions, despite their high contribution for COD [6, 20]. For that reason, usually, lipids are separated and used to produce biodiesel instead of using to VFAs production [20].

Commonly, carbohydrates are easily converted into glucose and then fermented to VFAs [20]. However, the carbohydrate fraction, that is not readily degraded (cellulose, lignin or hemicellulose), can affect the VFA production rate, as well as the VFA concentration and yield (**Table 1**).

Zhang et al. [25] observed that high content of readily degradable carbohydrates promotes a faster production of VFAs, while the presence of not readily degraded fraction (e.g., cellulose) can delay the production of VFAs or even lead to a lower production. Another study, showed that different FW (cheese whey, sugarcane molasses and olive mill effluent) resulted in different VFAs production (**Table 1**) and also different acidification degree (cheese whey and sugarcane molasses: up to 40%; olive mill effluent: up to 12%) [39].

The type of carbon source and its composition (e.g. carbohydrates, lipids, proteins) lead to different acidogenic metabolic pathways and, consequently, different VFAs composition. Indeed, in Zhang's study [25], according to the VFA profile, different fermentation type were obtained (**Table 1**). Silva et al., [39] observed that for the readily fermentable wastes (cheese whey and sugarcane molasses), acetic

FW	Y_{VFA}/s	VFA concentration	Dominant VFA	Ref.
Potato peels	452 mgCOD/gVS$_{feed}$	NA	Propionate (30.6%)	[25]
Carrots	321 mgCOD/gVS$_{feed}$	NA	Butyrate (54%)	[25]
Celery	372 mgCOD/gVS$_{feed}$	NA	Mixed acid	[25]
Chinese cabbage	201 mgCOD/gVS$_{feed}$	NA	Acetic acid (~40%)	[25]
Cheese Whey	NA	3374 ± 138 mgCOD/L	Acetic acid (~50%)	[39]
Sugar cane molasses	NA	3110 ± 124 mgCOD/L	Acetic acid (~50%)	[39]
Olive mill effluent	NA	934 ± 113 mgCOD/L	Acetic acid (~70%)	[39]
Tofu	0.16 g/gVS	7.28 g/L	Acetic acid (56.3%)	[20]
Egg white	0.26 g/gVS	15.23 g/L	Mixed acid (~25% of each)	[20]

VS – volatile solids; NA – not available; Ref. - reference.

Table 1.
VFA production from FW using mixed microbial cultures.

acid was the main acid produced, followed by butyric acid (26–28%) and caproic and iso-valeric acids (10–14%), while for the waste with low acidogenic potential (olive mill effluent), acetic acid was followed by propionic acid (21–24%) and the production of heavier VFA (e.g., butyric, valeric acids) was not detected.

Proteins have a complex structure, making them less suitable to protease action and, consequently, a lower hydrolysis efficiency [6, 20]. Indeed, the hydrolysis of carbohydrates can be up to 80%, while protein hydrolysis is between 40% to 70%, which leads the latter to be considered the rate-limiting step in AF [6]. As carbohydrates, the origin of proteins affects the production and composition of VFAs. Shen et al., [20] obtained a high production of VFA using animal protein when compared with vegetal protein (**Table 1**). Independently of the protein, animal and vegetal, acetic, propionic, butyric and valeric acids were produced. However, the acids profile is different in the fermented vegetal and animal protein. This difference in composition can be related to the type of amino acids present in tofu and egg white. Even though it has been demonstrated that the carbon source affects the VFA production, FW feedstocks with similar compositions must still be individually investigated, as other factors, like operational conditions, should be considered.

4.2 pH

pH is one of the most important and critical parameters in VFA production, since it affects VFA concentration and composition due to its influence in hydrolysis and acidogenic process [3, 5]. pH affects the microorganisms activity since most of the enzymes cannot tolerate low or high pH environments (pH < 3 or pH > 12) [2, 5]. Moreover, pH can also promote the inhibition of methanogenic activity, since operating the reactor out of their optimal range (7.0–8.2), the methane production can be inhibited [33]. The optimal pH for VFA production depends on the type of waste and should fit both hydrolysis and acidogenic steps [2, 5]. Indeed, different wastes present different optimal pH for VFA production (**Table 2**).

FW	Operating conditions	Optimal pH	[VFA]$_{max}$	VFA composition HAc/HPr/HBut/ others (%)	Ref.
Tuna waste	Batch; 37 °C; RT 39 days	8	30.61 g COD/L	60/11/14/15	[15]
FW (canteen)	Batch; 35 °C; RT 10 days	9	10.9 g/L	60.5/4.6/12.8/22.1	[33]
Potato peel waste	CSTR batch; 37 °C; RT 5 days	7	41.9 g COD/L	46/29/24/1	[19]
FW (canteen and market)	semi-continuous reactor; 37 °C; HRT 2d	9	18.19 ± 0.72 g/L	37.9/12.3/46.8/3.0	[34]
FW and waste activated sludge	Batch; 20 °C; RT 12 days	8	8.24 gCOD/L	31.9/51.8/9.2/7	[26]

RT – retention time; HAc – acetic acid; HPr – propionic acid; HBut – butyric acid; others can include valeric acid, iso-butyric and iso-valeric acid, caproic acid or not VFA; Ref. - reference.

Table 2.
Optimal pH for VFA production from different carbon source.

Bermúdez-Penabad et al. [15] studied the effect of low (5 and 6), neutral (7) and alkaline (8, 9 and 10) pH in the acidogenic fermentation of tuna waste and obtained the highest VFA production under alkaline conditions, achieving the highest production at pH 8. Although, the highest hydrolysis was also obtained under alkaline conditions, indicating that more substrate is available for acidification, strong alkaline conditions (pH 10) seem to affect the acidogenic bacteria activity since the ratio VFA/sCOD was the lowest one. Acetic and butyric acids were the main VFAs produced (except for pH 10). The increase of pH from 7 to 10 led to a decrease of the butyric acid content, while the change of pH from 5 to 8 led to an increase of acetic acid. Another study, using FW from canteen as feedstock, also observed the highest VFA production at alkaline pH (9), being acetic acid the dominant acid (60.5%) [33]. Hussain et al., [14], using solid FW from cafeteria as feedstock, operated four thermophilic leach bed reactor in batch mode under pH 4–7 and observed an increase of VFA production with pH increase (from 6 gCOD/L to 36.5 gCOD/L, corresponding a maximum yield of 247 g COD/kg TVS$_{added}$). At all pH, acetic and butyric acids accounted to 80–85% of the total VFA, being acetic acid the main produced acid at pH 4 and 5 (55–61%) and butyric acid the dominant compound at pH 6 and 7 (48–54%). On the other hand, Ma et al., [38], using FW from cafeteria, obtained the highest production of VFA at pH 6 (53.87 g/L), with a significant production of propionic acid. The fermentation of potato peel waste showed a different trend of VFA composition, since butyric acid was the main compound at acidic (pH 5) and uncontrolled pH, while acetic acid was the main compound produced at alkaline and neutral pH [19]. Moreover, the highest production of VFA was achieved at pH 7 (41.9 gCOD/L and 0.63 gCOD/gVS$_{fed}$). Stein et al., [34] studied the effect of pH, temperature and HRT on the maximization of the butyric acid production. pH 9 led to the highest production of VFA, as well as the highest VFA yield (0.726 gVFA/gVS$_{fed}$), which was about 80% higher than the yield obtained at pH 7. Besides butyric acid, that was the dominant compound at pH 9, acetic acid was also produced as the dominant compound (**Table 2**) and was the dominant

compound at pH 5.5 and 7 (34.8% and 47.9%, respectively). Propionic and iso-butyric acids were also produced. However, their content decreased at the highest pH tested. Wang et al., [23] studied the effect of pH (4, 5, 6 and uncontrolled) on the VFA production with two different inoculums (aerobic and anaerobic activated sludge). Regardless of the inoculum, VFA production was highest at pH 6, achieving a maximum of 30.8 gCOD/L (0.482 g/gVSS$_{removal}$, after 4 days of fermentation) and 51.3 gCOD/L (0.918 g/gVSS$_{removal}$, after 20 days of fermentation) for aerobic and anaerobic inoculum, respectively. Butyric acid was the dominant acid at pH 6, followed by acetic and propionic acids. Moreover, acetic and butyric acids were the predominant acids in all the pH tested, except for pH 4 and uncontrolled pH for aerobic inoculum, where acetic and propionic acids were the prevalent acids. Gouveia et al. [8] studied the impact of a dynamic variation of pH from 4 to 7, returning to pH 6 after each pH variation, in cheese whey derived-VFA production process. The production of organic acids was quite constant for all pH tested (about 13 gCOD/L), apart from pH 4 (about 4 gCOD/L). At pH 6, acetic acid was the main VFA, comprising 22–44%, and regardless of the dynamic variation of pH, the composition was always similar at pH 6. At high pH, the production of acetic acid was favored. Feng et al., [26] tested different pH (4–11) at room temperature and observed the highest concentration of VFAs at pH 8 (8.24 gCOD/L at 4 days of fermentation) during the co-digestion of FW with WAS. Acetic, propionic and butyric acids were the most prevalent VFA produced, achieving a total content of 82.5%, 91.9% and 92.9% at pH 5, 7 and 8, respectively. From pH 6 to 10, propionic acid was the main compound produced, while for pH 4 and 5, acetic acid was the main compound.

The pH effect on VFA production and profile using mixed cultures and FW does not present a direct relationship, being also dependent of the type of substrate used.

4.3 Temperature

Temperature is a key parameter that impacts the growth of microorganisms and their metabolism. Each microbial taxon has an optimal temperature range for its growth, and, therefore, a change on the operating temperature can affect the microbial population involved in the acidogenic fermentation [5, 6]. Mesophilic condition (25–45 °C) showed a similar or even higher VFA yield than thermophilic (50–60 °C) or hyperthermophilic (>65 °C) conditions [5]. On the other hand, thermophilic and hyperthermophilic conditions results in a higher hydrolysis and solubilization in comparison with mesophilic condition, which can lead to an increase of VFA production if an adequate microbial community is present [2, 13]. The composition of VFAs is also affected by the temperature, but in a less extent than that was observed for pH [2, 5]. The increase of temperature from mesophilic to thermophilic conditions leads to the metabolic shift from acetic acid to butyric acid [13]. Jiang et al. [36] reported that sCOD increased with temperature increase. However, the VFA concentration and yield at 55 °C was much lower than that obtained at 35 °C and 45 °C (14.90 g/L and 0.137 g/gVS$_{fed}$, 41.34 g/L and 0.379 g/gVS$_{fed}$, and 47.89 g/L and 0.440 g/gVS$_{fed}$, for 55, 35 and 45 °C, respectively), indicating a higher solubilization but a lower acidogenesis of FW at thermophilic condition (55 °C). The temperature increase resulted in a decrease of acetic and valeric acids content and an increase of butyric acid content. Acetic and propionic acid were the major compounds at 35 and 45 °C, representing ca. 70% of the total of VFAs. At 55 °C, butyric acid was the main compound, comprising more than 81% of the total VFAs and valeric acid was not detected. Although a higher ratio of VFA/COD and VFA concentration was observed at 45 °C, a high amount of energy is necessary to operate at this temperature. As such, 35 °C is considered as being the most cost-effective temperature

for FW derived-VFA production process [36]. Similarly, He et al., [37] observed a decrease of VFA concentration, from 17 to 11 g/L, when the temperature increase from 35 to 55 °C. At 70 °C, the VFA production (about 13 g/L) was higher than 45 °C but lower than 35 °C. The hydrolysis rate was directly affected by temperature, having increased with temperature increase, indicating that higher temperatures promote the hydrolysis of FW. Comparing the three temperatures, acetic acid was the main compound at 70 °C, iso-butyric and butyric acids were the main compounds at 55 °C, while ethanol was the main compound at 35 °C, showing that the increase of temperature can inhibit ethanol production, favoring the production of VFAs, namely acetic and butyric acids. Zhang et al. [35], who have studied the effect of two temperatures (35 and 55 °C) at different pH (5, 6 and 7), reached the maximum VFA yield of 11.8 gCOD/L at pH 7 and 35 °C, being acetic, propionic and butyric acids the main produced VFAs (about 80% of total VFAs). For each initial pH applied, mesophilic conditions led to higher VFA concentration. When comparing all the conditions tested, except for pH 7 and 55 °C, thermophilic temperatures led to lower VFA production than mesophilic conditions. Applying the optimal conditions to a continuous reactor, an average VFA concentration and yield of 6.3 gCOD/L and 0.29 gVFA/gVS$_{added}$ was obtained.

Temperature (37, 55 and 70 °C) also affected the maximization of the butyric acid production [34]. Higher temperatures led to a decrease of VFA concentration, namely in butyric acid concentration, except at pH 7 and 55 °C, where an 280% increase of butyric acid concentration was achieved when compared to mesophilic conditions. The maximum concentration of butyric acid was achieved at pH 7 and 55 °C (10.55 g/L ± 0.17) and pH 9 and 37 °C (8.52 g/L ± 0.10).

Considering operating costs, mesophilic conditions (25–45 °C) are the most economical and efficient temperatures to produce VFAs.

4.4 Organic loading rate (OLR)

OLR corresponds to the amount of substrate, in this case FW, fed to the reactor per day and per unit of working volume and can be expressed in terms of COD, total solids (TS), volatile solids (VS), volatile suspended solids (VSS) or dissolved organic carbon (DOC) [2]. The OLR increase promotes the production of VFAs, since more substrate is available [5]. However, the presence of inhibiting substances in the FW is a key factor that must be considered when operating at high OLR, as might affect the hydrolytic and acidogenic bacteria, as well as methanogens [7]. Several studies on the effect of OLR on VFA production from FW are summarized in **Table 3**.

Carvalheira et al. [1] observed the increase of VFA production (from 19.9 ± 5.0 gCOD/L to 34.4 ± 5.0 gCOD/L) and the change of VFA composition with the increase of OLR (from 21.2 ± 3.2 gCOD/(L.d) to 51.1 ± 8.8 gCOD/(L.d)) at HRT of 1 day. Under the lowest OLR, acetic and propionic acids were the major compounds (19.65% and 19.11%, respectively), while under the highest OLR propionic acid was the prevailing VFA (10.07%) (**Table 3**). Similarly, Jiang et al. [36] also observed the increase of VFA concentration with the increase of OLR. However, it was observed a decrease of VFA after 12 days of operation, under the highest OLR, indicating that an OLR of 11 gTS/(L.d) is more appropriate for VFA production from FW. Acetic and butyric acids were the dominant compounds accounting 60–65% of the total VFAs in all OLR applied. Acetic and valeric acids increased with the OLR, while propionic and butyric acids decreased with the OLR (**Table 3**). Teixeira et al., [21] studied the effect of OLR on VFA production using raw brewers' spent grain as feedstock and observed an increase of VFA concentration in about 2.5 times (**Table 3**). Regardless of the OLR, no significant effects on the VFA composition was observed, being propionic acid the dominant acid produced (**Table 3**).

FW	Operating conditions	OLR	VFA production	VFA composition Hac/HPr/HBut/HVal (%)	Ref.
Peach pulp waste	CSTR; HRT 1 day; 30 °C; pH 5.5	21.2 ± 3.2 gCOD/(L.d)	19.9 ± 5.0 gCOD$_{FP}$/L	19.65/19.11/14.38/9.88	[1]
		33.3 ± 4.2 gCOD/(L.d)	24.0 ± 3.2 gCOD$_{FP}$/L	16.42/18.16/10.01/5.01	
		51.1 ± 8.8 gCOD/(L.d)	19.9 ± 5.0 gCOD$_{FP}$/L	5.48/10.07/7.76/7.14	
Simulated FW	Semi-continous; HRT 5 days; 35 °C; pH 6.0	5 gTS/(L.d)	13.27 g/L; 0.504 g/gVS$_{fed}$	27.46/23.57/33.26/15.71	[36]
		11 gTS/(L.d)	21.44 g/L; 0.411 g/gVS$_{fed}$	34.07/17.70/31.00/17.23	
		16 gTS/(L.d)	24.93 g/L; 0.306 g/gVS$_{fed}$	36.55/14.70/28.62/20.12	
Raw brewers' spent grain	STR; HRT 19 days; 30 °C; pH 4.7	4.3 gTS/(L.d)	15.8 ± 2.0 gCOD$_{FP}$/L	29.7/44.5/11.4/12	[21]
	STR; HRT 16 days; 30 °C; pH 4.7	16 gTS/(L.d)	35.5 ± 3.5 gCOD$_{FP}$/L	28.2/41.3/17.2/9.6	
Mixture of different fractions of food waste	IMB; HRT 5 days; 37 °C; pH 5.5 (R1)	4 gVS/(L.d)	11.44 ± 1.09 g/L; 0.51 g/VS$_{added}$	Hac/HPr/HBut/HCap 42.51/<5/19.06/27.46	[22]
	IMB; HRT 10 days; 37 °C; pH 5.5 (R1)	8 gVS/(L.d)	27.40 ± 2.33 g/L; 0.44 g/VS$_{added}$	Hac/HPr/HBut/HCap 18.47/8.64/47.54/15.72	
	IMB; HRT 5 days; 37 °C; pH 5.5 (R2)	6 gVS/(L.d)	16.04 ± 0.84 g/L; 0.52 g/VS$_{added}$	Hac/HPr/HBut/HCap 39.52/5.67/23.6/24.94	
	IMB; HRT 10 days; 37 °C; pH 5.5 (R2)	10 gVS/(L.d)	36.99 ± 1.68 g/L; 0.46 g/VS$_{added}$	Hac/HPr/HBut/HCap 25.80/8.9/37.43/12.95	

CSTR – continuous stirred tank reactor; STR – stirred tank reactor; IMB – immersed membrane bioreactor; FP – fermented products; Hcap – caproic acid; HRT – hydraulic retention time; NA – not available; Ref. – reference.

Table 3.
Effect of OLR on VFA production using FW as substrate.

From the fermentation of different fractions of FW, the main compounds were acetic, caproic and butyric acids (**Table 3**), observing an increase of butyric and propionic acid and a decrease of acetic and caproic acids with the increase of OLR (**Table 3**). Moreover, the high production of acetic and butyric acids can be related to the high OLR applied, since these acids have been related to reactor overloading during anaerobic digestion processes [22].

OLR also influences the composition of VFAs, however it has to be correlated with other factors, such as pH and HRT, which also affects the VFA composition [2].

4.5 Hydraulic retention time (HRT)

HRT can be described as the average length of time that the substrate and biomass remain inside the reactor [6]. HRT should be long enough to promote the hydrolysis and the acidogenic fermentation steps, which depends on the type of FW [6]. In theory, high HRT is advantageous for VFA production since the microbial population has more time to convert the substrate. However, a very high HRT reduce the quantity of waste to be treated per day and can favor the methanogens activity, if suitable pH is applied [5, 6]. Moreover, high HRT can lead to VFA yield stabilization due to feedstock limitation [5]. The optimal HRT can vary even for the same feedstock [7]. Teixeira et al., [21] studied the effect of HRT (19 and 41 days) on the production of VFA at OLR of 4.3 gTS/(L.d). Due to the kind of substrate (solid and complex substrate without pre-treatment), high HRT was applied. The increase of HRT boosted the production of VFA (from 11.2 gFP/L to 24.4 gFP/L), since a longer contact between microorganisms and substrate was promoted. The prevailing acid produced was propionic acid, followed by acetic, butyric and valeric acids. However, their content was similar for both tested HRT, showing that HRT had no significant impact on the VFA composition. In another study, using a mixture of sewage sludge with cheese whey as feedstock, a sequential increase of HRT (from 10 to 20 days) was investigated [27]. The change of HRT increased the acidification degree (from 27 to 45%) with a similar ratio of VFA/sCOD (85 and 89%). The increase of HRT also promoted a slightly change on the VFA composition, with a slightly increase of iso-butyric and butyric acids (from 51 to 55%) and a decrease of acetic acid (from 33 to 24%). HRT depends not only on the type of substrate, but also on other operational parameters. As most of the studies are performed in batch reactors, the information about HRT effect on the VFA production is scarce.

4.6 Inoculum

The type of microorganisms present in the mixed microbial cultures may affect the acids production. It is necessary a careful selection of the microbial population present in the acidogenic fermentation process. If inadequate, a disparity on microbial populations can delay or limit the fermentative reactions and pathways, lowering the process yields [13]. Anaerobic inoculum from anaerobic sludge digesters obtained higher FW hydrolysis and VFA yield than aerobic inoculum from activated sludge process [13]. Atasoy et al. [40] investigated the effect of three types of inoculum with two different physical sludge structure (small and large granular sludge and anaerobic digester sludge) on VFAs production and composition. The highest VFA production was obtained with large granular sludge (1.99 ± 0.06 gCOD/L), followed by anaerobic digester sludge (1.14 ± 0.07 gCOD/L) and small granular sludge (1.06 ± 0.12 gCOD/L). As for VFA production, large granular sludge led to the highest VFA yield (0.97 gVFA/g$_S$COD). For small granular and anaerobic digester sludge a similar yield was obtained (0.36 and 0.38 gVFA/g$_S$COD, respectively), indicating that VFA production efficiency changed with the inoculum type.

Moreover, this study showed the ability of granular sludge to attain high VFA production efficiencies instead of biogas production, which is the usual application for granular sludge. Butyric and propionic acids were the main VFAs produced using large and small granular sludge, respectively, while acetic and propionic acids had similar content with anaerobic digester sludge. Wang et al. [23] studied the effect of pH (4.0, 5.0, 6.0 and not controlled) using two types of inoculum (anaerobic and aerobic). The highest VFA concentrations were obtained at pH 5.0 and 6.0, independently of the inoculum. Moreover, when anaerobic inoculum was used, it was obtained a slightly higher VFA production when compared with aerobic inoculum, which could be related to a higher acidogenic bacteria content present in the anaerobic inoculum and higher microbial activities under anaerobic conditions. Acetic and butyric acids were the main compounds (representing 90% of total VFAs) in all experiments except at pH 4.0 and not controlled pH using aerobic inoculum, where acetic and propionic acids were the major acids produced. Another study [13] evaluated the effect of inoculum source (mesophilic anaerobic sludge from biosolids digester of a municipal wastewater treatment plant (35 °C), thermophilic anaerobic sludge treating flour residues (55 °C) and hyperthermophilic anaerobic sludge treating microalgae) on the production of VFAs under mesophilic, thermophilic and hyperthermophilic conditions (70 °C). The mesophilic and thermophilic reactors were also operated at 70 °C. The hydrolysis efficiency was similar for all reactors, ranging between 27 and 40%. The reactor operation obtained under thermophilic conditions led to the highest fermentation yield (0.44 gCOD/gVSS-COD$_{added}$), followed by mesophilic (0.33 gCOD/gVSS-COD$_{added}$) and hyperthermophilic conditions (0.08 gCOD/gVSS-COD$_{added}$). Moreover, the fermentation yield at 70 °C using mesophilic and thermophilic were lower than that obtained at standard conditions (0.30 gCOD/gVSS-COD$_{added}$ and 0.28 gCOD/gVSS-COD$_{added}$, respectively). VFAs accounted to ca. 60–71% of the solubilized matter at mesophilic and thermophilic conditions, with acetic acid the major compound (70%) at mesophilic temperature and butyric acid (60%) the major compound at thermophilic temperature. The higher production of VFA at 35 °C and 55 °C revealed the importance of inoculum source in the improvement of acidogenic activity. Thus, different inoculum types present a variability in microbial populations which lead to a distinct performance of hydrolytic and acidogenic processes.

4.7 Pre-treatment

The pre-treatment will make the complex compound of FW more accessible for the hydrolysis, being the rate-limiting step of fermentation process.

Pre-treatments can be divided in physical, chemical and biological categories [41]. Physical pre-treatment present the high efficiency in terms of degradation but present high costs related to high energy consumption. Chemical pre-treatment is a cheap and efficient process but is not environmentally appealing and the chemicals used may cause fermentation inhibition. Biological pre-treatment presents several advantages (natural process, environmentally friendly, non-toxic for fermentation, economic) but are slower than physical and chemical processes.

Physical pre-treatment comprises heat, mechanical and radiation processes to change the structure and/or composition of FW. In terms of chemical pre-treatment the most commonly used are alkaline or acidic solutions, hydrogen peroxide and ozone. Alkaline and acidic pre-treatments break the cell wall promoting the solubilization. However, these pre-treatments may cause equipment corrosion and interfere with the fermentation pH. Ozone pre-treatment is safer but expensive. Hydrogen peroxide is toxic for the environment and causes cell growth inhibition, even though it presents a high solubilization degree [41]. Biological pre-treatment

comprises microbial (inoculated microorganisms as single culture or consortia and microorganisms from matured compost) and enzymatic (single or mixed enzymes) pre-treatment. Enzymatic pre-treatment is faster than microbial pre-treatment. However, it can be a costly treatment due to the operating costs involved in the production and extraction processes [41].

Guo et al., [18] evaluated the effect of different pre-treatments (sulfuric acid, acetic acid, aqueous ammonia, sodium hydroxide and steam explosion) of corn stalk on the production of organic acids. Steam explosion was the most suitable process for microbial growth and VFAs production, achieving a total of 2.98 g/L. The lowest production of VFAs was achieved using the acetic acid pre-treatment. Shen et al. [20] investigated the effect of hydrothermal pre-treatment (160 °C and 30 minutes), on tofu and egg white and assessed the production of VFAs using the pre-treated and untreated feedstock, observing that the pre-treatment improved the VFA production from tofu but not from egg white. Treated tofu reached a maximum VFA concentration of 21.07 g/L and a yield of 0.46 g/gVS, while with treated egg white a maximum VFA concentration of 11.45 g/L and a VFA yield of 0.20 g/gVS were achieved. Contrarily to the VFA yields, the VFA composition was not affected by the hydrothermal treatment. Yin et al., [24] also assessed the effect of hydrothermal pre-treatment (140, 160, 180 and 200 °C and 30 minutes) on the production of VFAs from FW. The hydrothermal pre-treatment of FW enhanced the VFA production. The optimal hydrothermal temperature was at 160 °C, where a VFA yield of 0.908 g/gVS$_{removal}$ and a VFA concentration of 34.1 g/L (increase of 47.6% compared with control) was reached. Independently of pre-treatment temperature, butyric and acetic acids (between 38.6–41.2% and 31.1–35.2%, respectively) were the dominant acids, followed by propionic acid (about 20%) and valeric acid (about 8%, except for pre-treatment at 200 °C (14.51%)). Pre-treatment of FW is one option to achieve high solubilization, improving the FW biodegradability and consequently enhance the VFAs production.

4.8 Other factors

Other factors, such as total solids (TS) [15, 42], co-digestion [43] and substrate shift [16, 17] also affect the VFA production.

The initial total solid (TS) concentration can limit the mass transfer between the substrate and the microorganisms [42]. Wang et al., [42] tested four initial TS concentrations (40, 70, 100 and 130 g/L) observing a slower VFAs production at higher TS concentration, although a higher VFA concentration was obtained (62.24 gCOD/L). The increase of TS content, from 40 to 130 g/L, led to a maximum VFA concentration of 26.10, 39.68, 59.58 and 62.64 gCOD/L. On the other hand, the increase of TS content led to a decrease of VFA yield (0.799, 0.644, 0.604 and 0.467 gCOD/gVS$_{fed}$) and acidification degree (48.2%, 42.7%, 41.2%, and 35.8%). Propionic acid accounted to 30.19–34.86% of the total VFAs and was not affected by the TS concentration, while a higher content of butyric acid and a lower content of acetic acid were achieved at higher TS content. Bermúdez-Penabad et al., [15], also observed an increase of VFA concentration with the increase of TS content (from 2.5 to 8%TS (w/v)) and obtained the higher VFA yield and acidification at lower TS concentration (0.73 gCOD$_{VFA}$/gCOD$_{waste}$ and 73%, respectively). The lower yields at higher TS content could be related to inhibition at high VFA concentration. Independently of TS content, acetic acid was the dominant acid produced, followed by butyric, iso-valeric and propionic acids.

Co-digestion consists in the simultaneous treatment of two or more substrates. Although the mono-digestion of FW is suitable, co-digestion presents several advantages and benefits, like as an improvement of nutrients balance, synergistic

effects between microorganisms, dilution of potential toxicity, increase of digestion rate [10, 26]. FW can be mixed with different other wastes to improve the system performance [10]. In Feng's study [26] an improvement in VFA production was obtained by the addition of FW to waste activated sludge fermentation. The production of VFA with only waste activated sludge or FW was 971.7 and 1468.5 mgCOD/L, respectively, while in the co-digestion increased to 8236.6 mgCOD/L. Moreover, the VFA composition obtained from waste activated sludge or FW fermentation was different than that obtained in the co-digestion, although acetic and propionic acids were the prevalent acids produced. Another study [27] also showed that the increase of cheese whey content on the sewage sludge digestion increased the production of VFAs. Using only sewage sludge as substrate the maximum concentration obtained was 1507 mgCOD/L, while the addition of cheese whey, in a ratio of 25:75, allowed to increase the VFA concentration up to 3226 mgCOD/L. The addition of cheese whey also led to a changed in the VFA profile, with acetic, propionic and butyric acids being the main acids produced, while acetic, propionic and iso-valeric acids were the prevalent acids produced in sewage sludge fermentation.

Most of the wastes are seasonal which can affect the continuous production of the VFAs. So, two possible solutions may be used: (1) feedstock storage or (2) feedstock shift. In the first option, the storage might require huge buffer tanks or facilities, besides the possible feedstock degradation during the storage. In the second option, the change between different feedstock could led to a different VFA composition and production, besides could affect the robustness of the continuous operation. Duque et al., [17] studied the feedstock shift from cheese whey to sugar cane molasses to cheese whey, observing an immediate response to the feedstock shift by the change of fermented products profile. The highest fermented products concentration (13.2 gCOD/L) was achieved using sugar cane molasses, being propionic and valeric acids the most prevalent compounds. During the operation with cheese whey, a maximum concentration of fermented products of 9.7–10.6 gCOD/L was achieved, being acetic and butyric acids the dominant compounds. Although the feedstock shift from cheese whey to sugar cane molasses changed the fermented products concentration and composition as well as the kinetic parameters, the shift from SCM to cheese whey demonstrated the process robustness since the system responded similarly to the first cheese whey. Mateus et al., [16] assessed the effect of the feedstock shift and operational conditions (pH and OLR/HRT) of three pulp waste (peach, raspberry and white guava) on acidogenesis. The authors observed that, independently of pulp composition, the fermented products profiles were similar and stabilized over a short period of time after each operation change (feedstock shift or operational conditions), showing the robustness of the system. Butyric, acetic and valeric acids were the main acids produced in all the conditions tested. Generally, the latter studies showed the ability of the microbial community to deal with FW feedstock shift with no need to stop the operation, representing an important advantage at full scale operation.

5. Applications of VFAs

VFAs are valuable products with a huge market demand and a wide range of applications such as polyhydroxyalkanoates, biodiesel, biogas, biohydrogen, and biological nutrient removal [2, 3, 5].

5.1 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are thermoplastic biodegradable polyesters produced by microorganisms from renewable resources, such as VFAs [2, 29].

PHA has a wide range of applications, such as packaging, compost bags, agriculture/horticulture films, durable and consumer retail goods [29] and besides to be environmental-friendly, their implementation has been limited due to the high production cost when compared with the conventional plastics [2, 17]. Usually, industrial PHA production use pure cultures and expensive substrates (e.g., sucrose or glucose), so it is expected that the combination of mixed microbial cultures, which do not require sterile conditions, and low-cost substrates, such as VFAs from FW, will contribute for the decrease of operational costs due to reduction of substrate cost and saving energy [17, 29]. PHA production from mixed microbial cultures comprises three-stages: (1) acidogenic fermentation, where the organic matter is converted into VFAs; (2) selection of mixed microbial cultures, where the microbial culture is enriched in PHA accumulating organism; (3) PHA production, where the mixed microbial cultures selected in the second stage is fed with the VFAs produced in the first stage at the culture's maximum PHA accumulation [3, 17]. Using this process, a PHA content of 40–77% can be achieved from fermented FW [2]. The VFA composition establishes the PHA composition, which defines the physical and mechanical properties of the polymer. Acetic and butyric acids are converted into polyhydroxybutyrate (PHB), while propionic and valeric acids are converted into polyhydroxyvalerate (PHV). PHB is the most common PHA produced, however due to their properties (brittle and stiff), present limited applications [2, 29]. The incorporation of HV monomers result in a co-polymer (P(HB-co-HV)), which is more flexible and tougher [2].

5.2 Bioenergy

The increase of energy demand, as well as the depletion of oil reserves have been led to the development of suitable alternatives for energy resources. Waste-derived VFA is a low-cost source for the generation of different types of energy, such as biogas, biohydrogen or biodiesel (valuable fuels).

5.2.1 Biogas

Biogas, the final product of anaerobic digestion, is mainly composed by methane so it can be used as green energy source (energy value of 37.38 kJ/L) for heat and power generation [16]. The most anaerobic digestion processes use a single reactor, where VFAs are the intermediate product. However, acidogens and methanogens are not subjected to their optimal growth and activity conditions, which can affect the system performance [1, 2]. In order to provide the optimal conditions for the microorganisms and avoid the methanogens inhibition, due to a quick acidification of FW, a two-stage system can be used. In this case, the hydrolytic/acidogenic stage is separated from the methanogenic stage [1, 16]. Hydrolytic/acidogenic stage can be operated at acidic pH and low HRT, producing VFAs and hydrogen, while the methanogenic stage can be operated at neutral pH and high HRT, producing biogas rich in methane from the VFAs obtained in the first stage [1, 2]. Among all the VFAs, propionic acid is the main acid that can negatively impact the methanogenic activity, and consequently the biogas production, at concentrations above 1.36–2.27 gCOD/L [16].

5.2.2 Biohydrogen

Hydrogen is considered the future fuel and one of the most attractive renewable energy due to their efficiency characteristics [6]. Biohydrogen can be produced in the first stage of the two-stage anaerobic digestion process and can be used as a

renewable energy source (energy value of 12.71 kJ/L), boosting the energy recovery of the process [16]. Biohydrogen production potential is affected by the content on carbohydrates, as these are the preferred substrates for hydrogen production [16].

Biohydrogen can be also produced by photo fermentation, where the conversion of VFAs into hydrogen is performed by purple non-sulfur bacteria in the presence of light and using several organic compounds as feedstock [44]. Inhibitory compounds of FW, temperature, pH, wastewater color, light intensity and wavelength can affect the hydrogen production [44]. Moreover, the type of carbon also affects the efficiency of the process, due to the variation in electron transfer capabilities in different metabolic pathways [44].

5.2.3 Biodiesel

Biodiesel is a methyl ester of long-chain fatty acids, which can be obtained from lipids through transesterification process. Biodiesel is a renewable energy source, however its production presents high costs due to the use of costly raw materials (about 70–75% of the total cost) [2]. Therefore, the production of biodiesel from waste-derived VFA have been gaining attention, where the VFAs can be converted into microbial lipids for biodiesel production [3]. The utilization of VFA as feedstock resulted in high lipids production and yield, showing the ability of VFA to produce lipids. VFA composition, pH, temperature, strains, inoculum concentration and nitrogen to carbon ratio can impact the lipids production [3].

5.3 Biological nutrient removal

Biological nitrogen removal is a biological process that includes aerobic nitrification followed by anoxic denitrification for the nitrogen removal. It is known that VFAs are an important carbon substrate for nitrogen removal, representing an economical alternative as feedstock for denitrification. Moreover, phosphorus can be removed by enhanced biological phosphorus removal process, where the microorganisms are subjected to anaerobic and aerobic conditions and VFAs are used as carbon source. Alternating between anaerobic-aerobic-anoxic conditions, a simultaneous nitrogen and phosphorus removal can be achieved [2, 3]. The denitrification efficiency and rate can be influenced by the composition of VFA stream, being acetic and propionic acids the preferred acids due to their high nitrate removal rates [3]. On the other hand, propionic acid present a high phosphorus removal efficiency [2]. Besides the type of VFA, other operational parameters, such as type of reactor/process, dissolved oxygen, temperature, and pH can affects the efficiency of biological nutrient removal process.

6. Conclusion(s)

The biological production of VFAs from FW is one of the most promising sources for resource recovery due to the high availability of this waste. The production and recovery of VFAs from waste will accomplish one of the goals for this century, allowing to reduce the consumption of raw materials, as well as the waste accumulation/pollution and is in line with the circular economy approach by the substitution of the linear economic model of "take-make-consume-dispose" by the circular economy model. It has been demonstrated that VFAs have a great potential to be used for several applications, such as PHA and bioenergy production. Several process conditions (e.g. type of FW, pH, HRT, OLR, temperature, etc.) affects the VFA production in terms of VFA profile, concentration, and yield. Thus, these

factors must be taken into consideration when implementing this process to fit the final application. For instance, the acidogenic fermentation can be manipulated in order to produce different VFAs profiles, leading to PHAs with different compositions (taylor-made). At last, several pre-treatments can be applied to FW, enhancing the acidification process. However, positive and negative aspects must be considered when choosing the type of pre-treatment, namely costs and environmental concerns.

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Conflict of interest

The authors declare no conflict of interest.

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