Rev Environ Sci Biotechnol (2021) 20:439–478
https://doi.org/10.1007/s11157-021-09566-0

REVIEW PAPER

Current perspectives on acidogenic fermentation to produce volatile fatty acids from waste

Maria Ramos-Suarez · Yue Zhang · Victoria Outram

Received: 14 August 2020 / Accepted: 12 January 2021 / Published online: 13 February 2021

Abstract Volatile fatty acids (VFAs) are key platform chemicals used in a multitude of industries including chemicals, pharmaceuticals, food and agriculture. The current route for VFA production is petrochemical based. VFAs can be biologically produced using organic wastes as substrate, therefore directly contributing to a sustainable economy. This process is commonly known as acidogenic fermentation (AF). This review explores the current research on the development of AF processes optimized for VFA production. Three process steps are considered: feedstock pretreatment, fermentation, and primary product recovery with a focus on in situ recovery. Pretreatment is required for recalcitrant feedstocks, especially lignocellulosic substrates. Different pretreatment techniques for AF application have not been studied in depth. The operational parameters of AF (temperature, pH, hydraulic retention time, substrate concentration, etc.) highly influence microbial activity, VFA yields and product distribution. Optimum conditions are ultimately dependent on substrate composition, however, there is indication that certain operational ranges are beneficial for most feedstocks. VFA recovery and purification are necessary for chemical applications. When recovery is performed in situ, it can help relieve product-induced inhibition and keep alkalinity levels stable enabling further waste degradation. Many techniques have been tested, but none are directly compatible with the fermentation conditions tested. Bio-VFAs have the potential to aid in developing a circular economy, but further development is required. Processes need to be developed with the product market in mind, considering both process integration and systematic process optimization.

Keywords Acidogenic fermentation · Volatile fatty acids · Carboxylic acids · Product recovery · Waste feedstocks · Short chain fatty acids

1 Introduction

Volatile fatty acids (VFAs), or short-chain fatty acids (SCFA), normally refer to C2–C5 fatty acids. Table 1 shows the chemical properties of VFAs with some current market data. VFAs are platform chemicals used in a broad range of industries such as pharmaceutical, food, chemical and agriculture (Baumann

Supplementary Information The online version contains supplementary material available at. https://doi.org/10.1007/s11157-021-09566-0.

M. Ramos-Suarez · Y. Zhang · V. Outram (✉)
Faculty of Engineering and Physical Sciences, University of Southampton, Southampton, UK
e-mail: victoria.outram@nottingham.ac.uk

V. Outram
Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham, UK

Table 1 Volatile fatty acid chemical properties and market data

Acid	Chemical formula	Molecular mass (g mol^{-1})[a]	Density (g cm^{-3}) at 20°C[a]	Boiling point (°C)[a]	pKa[a]	Average price (USD kg^{-1})[b]	US production in 2016 (MT)[c]
Acetic (HAc)	CH_3COOH	60.052	1.05	117.9	4.76	0.89	1224–2449
Propionic (HPr)	CH_3CH_2COOH	74.079	0.99	141.1	4.88	2.20	11–17
Isobutyric (iHBu)	$(CH_3)_2CHCOOH$	88.106	0.95	154.4	4.84	2.75	–
Butyric (HBu)	$CH_3CH_2CH_2COOH$	88.106	0.96	163.7	4.82	2.55	1.13–2.27
Isovaleric (iHVa)	$(CH_3)_2CHCH_2COOH$	102.133	0.93	176.5	4.77	–	–
Valeric (HVa)	$CH_3(CH_2)_3COOH$	102.133	0.94	186.1	4.84	4.63	0.45–0.91

[a]Physical properties taken from PubChem Compound Database (Information National Center for Biotechnology 2018)

[b]Price data gathered throughout April 2018 from multiple sources (Alibaba 2018)

[c]Domestic production in the US in 2016 (United States Environmental Protection Agency 2016)

and Westermann 2016), with over 1.2 billion tonnes produced in 2016 in the US alone. VFAs are predominantly produced through chemical synthesis from petroleum-based feedstocks. This process typically involves high temperatures, high pressures and catalysts for conversion to VFAs (Dionisi and Silva 2016). Oil price instability, finite fossil fuel reserves and the need for a sustainable circular economy, however, are recurring arguments to promote a change from petrochemical production to bio-based processes.

Microbial processes can be used to produce VFAs; either through pure-culture fermentations for a targeted acid or using mixed-culture derived from anaerobic digestion (AD) for mixed VFAs. Microbial VFA production has the advantages of being able to use renewable feedstocks, generating safer products for human health, and offering high product selectivity (in pure culture) (Huang et al. 2007). Mixed-culture fermentation has advantages over pure-culture fermentation as a wider range of feedstocks can be used, including agricultural waste, food waste and wastewater sludges (Lee et al. 2014), as well as offering energy savings through operating under non-sterile conditions. To the authors knowledge, there are currently no commercial mixed-culture AF processes.

AD is a mature technology, and widely used for waste valorization towards biogas (methane and carbon dioxide) production for bioenergy. Low revenues from methane production make it economically unattractive for waste processing companies without subsidies (Smyth et al. 2010; Gebrezgabher et al. 2010; Dolan et al. 2011). Additionally, AD capital expense can be high due to the long retention times and large reactor volume needed to complete metabolic reactions. Consequently, there is a growing research focus on acidogenic fermentation (AF), sometimes known as dark fermentation, to produce VFAs. AF is derived from the first half of the AD process, Fig. 1, and produces a higher value-added product chain. AF can also produce hydrogen and carbon dioxide, further increasing the number of product streams (Kleerebezem et al. 2015).

In this review, the whole process for VFA production from potential market through to the current technology landscape for both the fermentation and primary recovery step is assessed. The current knowledge gaps and challenges which need to be investigated are highlighted, with the aim of progressing a commercially viable bio-VFA platform.

2 VFA uses from acidogenic fermentation

When designing a process, the VFA use needs to be understood, as this will influence the desired process and subsequent optimization. Figure 2 provides

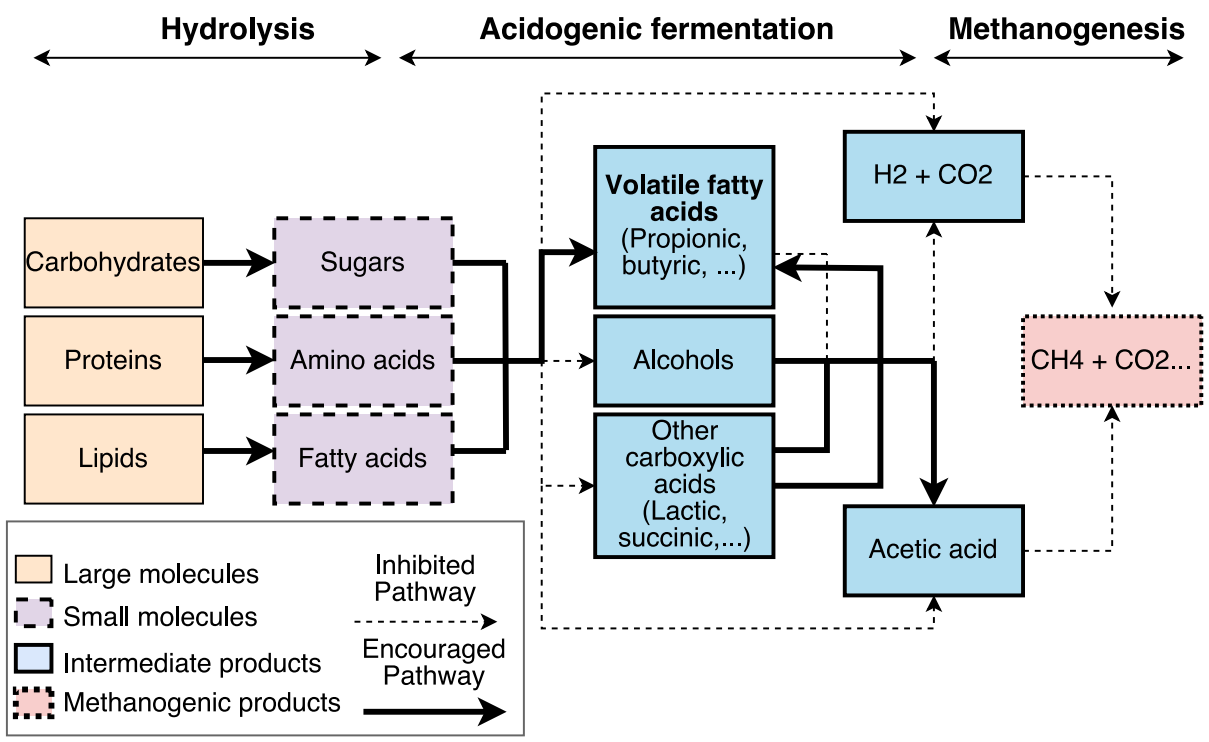

Fig. 1 Anaerobic digestion steps and pathways: encouraged pathways show the preferred metabolic routes for acidogenic fermentation towards volatile fatty acids production

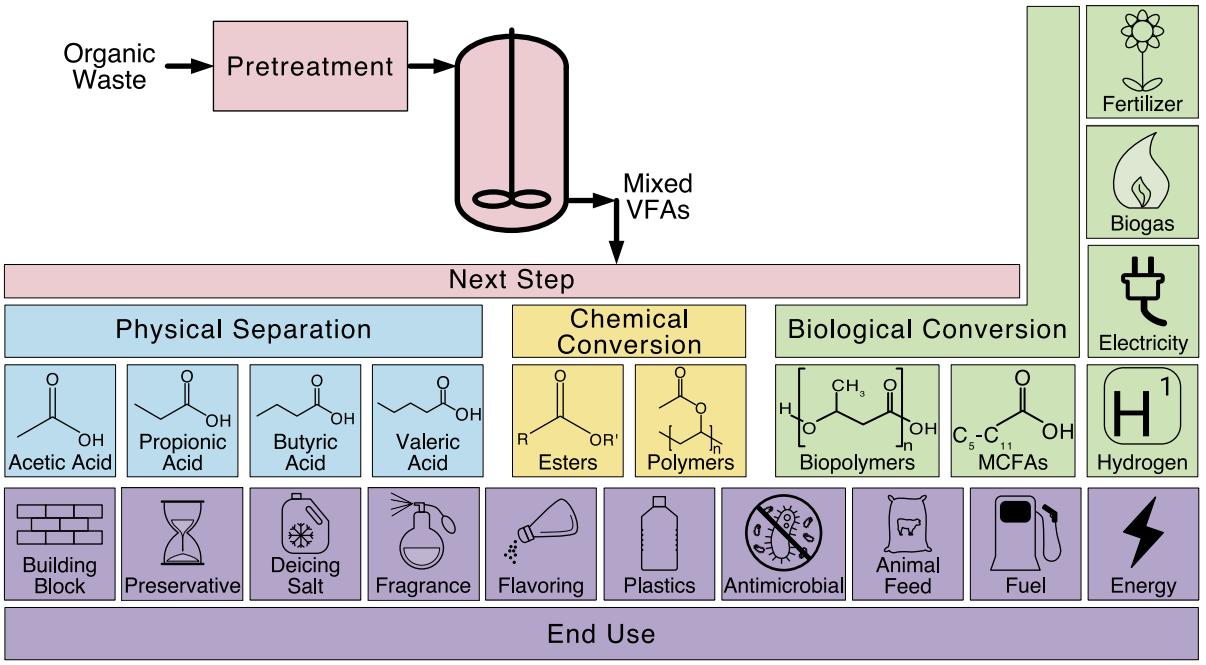

Fig. 2 Examples of potential uses and process options of mixed VFAs from acidogenic fermentation

examples of the possible end products that can be derived from VFAs, and the processing route required to make them from AF. The obvious use for bio-VFAs is as a direct substitute for existing petrochemical-VFAs. Production of bio-VFAs as an alternative to petro-VFAs poses some challenges with the separation of the individual acids from the mixed VFAs in water. This is due to the similar properties of all the VFAs (Table 1), the low concentrations achieved in the fermentation (1–100 g L^{-1}), and the potential for formation of water-acid azeotropes. An alternative to VFA separation is direct chemical conversion of the mixed VFAs, Fig. 2. Conversion of VFAs to esters has been considered by some groups (Cabrera-Rodríguez et al. 2015; Wallis et al. 2017; Plácido and Zhang 2018a). Another possibility could be polymerization of the VFAs for the production of plastics and other fibrous material such as polyvinyl acetate or cellulose acetate butyrate (Straathof 2014). There has been no research into polymerization of mixed VFAs to date.

The primary use of mixed VFAs considered in literature is as a feedstock for biological conversion. As Fig. 2 shows, this covers a wide range of possible uses as a feedstock for the production of polyhydroxyalkanoates (PHA); medium-chain fatty acids (MCFAs); bioenergy and electricity through microbial fuel cells; or for biological nutrient removal (BNR) in wastewater treatment which would produce a fertilizer (Bengtsson et al. 2008b; Mengmeng et al. 2009; Lee et al. 2014; Kleerebezem et al. 2015; Tao et al. 2016; Colombo et al. 2017; Bhatia and Yang 2017; Liu et al. 2018a; De Groof et al. 2019). The VFAs could be converted to biogas, through methanogenesis. This is the equivalent of a two-stage AD process, but with the addition of a separation stage to capture the VFA which is fed to the methanogensis stage (Lee et al. 2014). Alternatively, VFAs could also transformed into hydrogen as an energy carrier through photo-fermentation or microbial electrolysis (Uyar et al. 2009). Whilst there is scope for the conversion of VFAs into energy sources, this does not appear to be the most value-adding use of bio-VFAs as there are already proven and well-established technologies for biogas, electricity and hydrogen production from renewable sources.

3 Process overview

The production of VFAs can be simplified into three main steps: feedstock pretreatment, fermentation and product recovery, Fig. 3. The chosen waste can be pretreated to enhance hydrolysis and improve the biodegradability. It is then fermented using a mixed-culture to produce VFAs, along with hydrogen, carbon dioxide and soluble by-products, such as alcohols and other organic acids. Ideally, the fermentation will be a continuous process, with maximized yield and productivity. The recovery process can be integrated with the fermentation step to allow maximum carbon conversion to VFAs, therefore the VFA-depleted fermentation broth is recycled to the reactor. Only the primary recovery step is discussed in this review, as any subsequent steps depend on the chosen product use to determine optimal output streams or further purification requirements. The fermentation effluent is likely to contain some soluble compounds in addition to organic suspended solids, therefore still containing chemical oxygen demand (COD) which can be further processed by AD to maximize waste degradation and valorization. The fermentation gasses, CO_2 and H_2, can also be fed to the anaerobic digester for upgrading to methane (Tao et al. 2019).

3.1 Feedstock types

Any organic substrate can be used as feedstock for AF. The preference is for waste biomass (2nd generation) feedstocks avoiding the food vs fuel debate, as well as contributing to waste management strategies (Rulli et al. 2016), therefore this is the focus of AF processes and this review.

The most abundant solid wastes used in AD and AF include animal manure, agricultural residues, livestock residues, sewage sludge, waste activated sludge (WAS), organic fraction of municipal solid waste (OFMSW) and food waste. For liquid wastes; sewage, agroindustrial, chemical industry, food processing and pharmaceutical wastewaters have all been used (Mata-Alvarez et al. 2000; Weiland 2010; Lee et al. 2014; Kleerebezem et al. 2015; Bharathiraja et al. 2018). Recently, novel substrates such as (micro)algae biomass are gaining research interest (Li et al. 2013; Magdalena et al. 2018; Jankowska et al. 2018).

All substrates contain mostly proteins, fats, and carbohydrates. Most compounds in liquid waste are

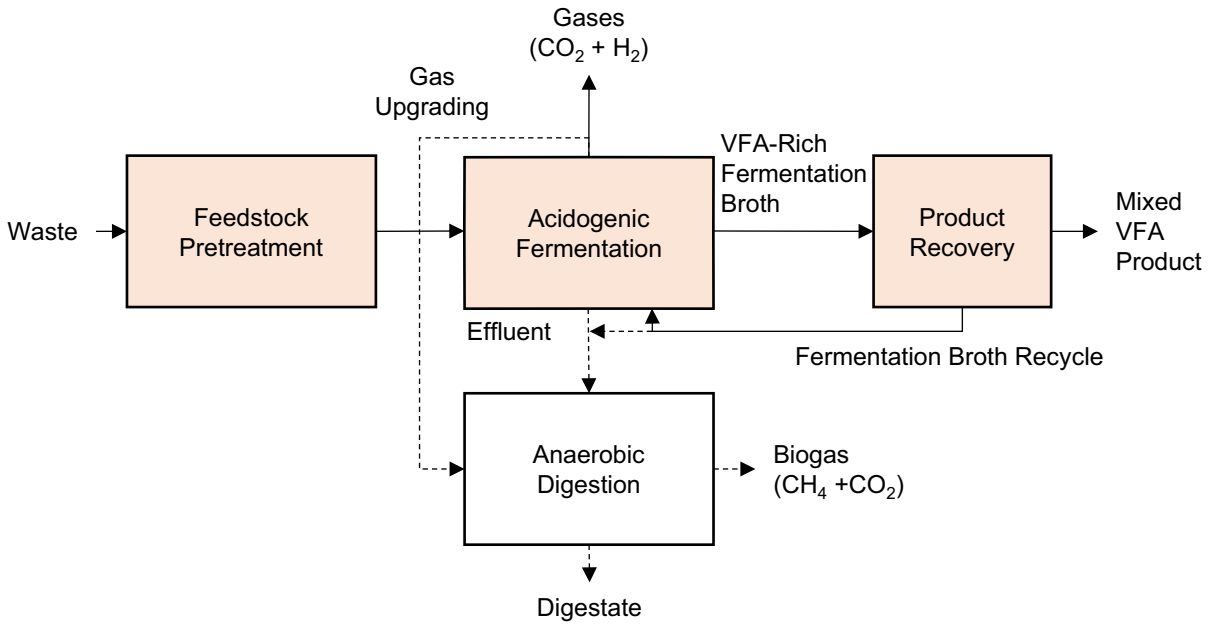

Fig. 3 Process flow diagram of VFA production via AF. Solid lines show process for maximized yield. Dashed lines show optional AD step to maximize waste valorization, gas upgrading and biomass disposal, if maximal yield is not techno-economically attainable

solubilized organics, but they can also contain suspended solids. Ideally, the feedstock has to be pathogen free and contain a balanced C/N ratio (30/1 to 15/1 recommended for AD) (Gerardi 2003; Paul and Dutta 2018). Animal manures generally have good buffering capacity and contain anaerobic microorganisms suitable for AD, eliminating the need of additional inoculum (Bharathiraja et al. 2018). Most solid wastes comprise a proportion of lignocellulosic material. The lignin structure hinders microbial degradation affecting AD efficiencies (Paul and Dutta 2018). Generally, wastes with high lignocellulosic content require pretreatment to ease the lignocellulose structure breakdown into soluble carbohydrates (Paul and Dutta 2018). This is the case with OFMSW and agricultural wastes. In addition to high lignin content, OFMSW is deficient in nutrients and contains inorganics (Bharathiraja et al. 2018), such as broken glass, grit, plastics and metals. The attractiveness of using algae as biomass for AD/AF reside is the high growth rates compared to terrestrial biomass, CO_2 uptake during growth and removal of nutrients from wastewaters (Bharathiraja et al. 2018). Algae does have drawbacks such as an unbalanced C/N ratio, compounds toxic to microorganisms, and relatively low biodegradability (Matsakas et al. 2017; Bharathiraja et al. 2018).

3.2 Pretreatment

Pretreatment of feedstocks is often required for AF (and AD), as many of the substrates are recalcitrant and do not readily degrade by the micro-organisms alone, e.g. lignocellulosic feedstocks (Romero-Cedillo et al. 2017). Pretreatment studies focusing specifically on VFA production are scarce. Pretreatment studies for AD could be used to infer possible options for AF, although these are not optimized for VFA production.

Pretreatments can be classified as mechanical, chemical, physical, physiochemical, and biological; with the aim to increase biodegradability by fragmenting the lignin, decreasing the cellulose crystallinity or hydrolyzing the carbohydrates into simpler molecules (Jönsson and Martín 2016). Pretreatment should result in acceleration of the hydrolysis stage and VFA yields improvement.

Pretreatment methods for AD have been extensively reviewed by Cesaro and Belgiorno (2014), Ariunbaatar et al. (2014), Romero-Cedillo et al (2017) and Bharathiraja et al. (2018). This review highlights

Table 2 Summary of pretreatment techniques with a focus on application to AF, based on available literature

Technique		VFA/H_2 increases demonstrated	Energy intensive	Most suited feedstock	Additional chemicals required	Accelerates hydrolysis	Toxic compounds introduced or made	Degrades fermentable sugars	Degrades lignin	Recovery/ neutralization treatment required	Expensive
Mechanical		Up to 30% increased solubility	No	Dry feedstock	No	–	No	No	No	No	No
Chemical	Acid treatment	Up to 370% increase in VFA yield	No	High protein wastes	Yes	Yes	Yes	Yes	No	Yes	Yes
	Alkali treatment	Up to 400% increase in VFA yield	No	Primary sludge and lignocellulosic waste	Yes	–	Yes	–	Yes	Yes	Yes
	Peroxidation	Not tested	No	–	Yes	–	Yes	–	Yes	Not for H_2O_2	Yes
	Ozonation	Up to 158% increase in H_2 yield	Yes	Lignocellulosic waste	No	–	Yes	Yes	Yes	No	Yes
	Organic solvents	Not tested	Yes	–	Yes	–	Low	–	–	Yes	Yes
Physical	Thermal treatment	Up to 380% increase in VFA yield	Yes	WAS	No	Yes	Yes	–	–	No	Yes
	Microwave	Small increases on VFA yields (< 30%)	Yes	Sludge	No	–	Yes	–	–	No	–
	Ultrasound	57% increased solubility	Yes	Only tested on WAS	No	–	Yes	–	–	No	–
	Focused pulsed	Not tested	Yes	MSW, WAS	No	–	–	–	–	No	–
Physio-chemical	Thermochemical	Up to 470% increased solubility	Yes	–	Yes	–	Yes	Yes	–	No	Yes
	Wet air oxidation	Not tested	–	Liquid wastes	No	–	–	–	–	–	Yes
	Ionic liquids	Not tested	Yes	–	Yes	–	Yes	–	Yes	Yes	Yes
	Ammonia fiber explosion	Small increases on VFA yields (< 30%)	–	Low lignin content	Yes	–	Low	–	Yes	–	Yes
Biological	Fungi	Not tested	No	–	No	–	No	Yes		No	No
	Extracellular Enzymes	Yes	No	–	No	Yes	No	–	Not if performed under sterile conditions	No	Yes

the pretreatment methods effectiveness for VFA production. The conclusions are summarized in Table 2.

3.2.1 Mechanical

Milling, grinding and chipping increases the surface area, improving biodegradability and solubility. In AD, excessive particle size reduction can accelerate VFA accumulation (Izumi et al. 2010; Cesaro and Belgiorno 2014; Romero-Cedillo et al. 2017). For food waste, smaller particle sizes (0.4 mm) trigger acetic acid production, whereas larger particle sizes (0.9 mm) favor butyric acid (Izumi et al. 2010). Advantages of mechanical treatments are that they require low energy for dry feedstocks, are simple to implement, and improves dewaterability of the waste. The disadvantages are that it does not degrade lignin, does not assist with pathogen removal (Romero-Cedillo et al. 2017) and has high equipment maintenance requirements (Cesaro and Belgiorno 2014).

3.2.2 Chemical

Acid treatment hydrolyses the hemicellulose. This treatment has demonstrated improvements in yield for hydrogen production, which can be correlated to VFA production, and has been proven more effective than other pretreatment options for protein rich wastes (Cesaro and Belgiorno 2014; Romero-Cedillo et al. 2017). For WAS, a 153% and 370% VFA yield increase was observed using hydrochloric acid (Wu et al. 2017) and free nitrous acid (Li et al. 2016), respectively.

Alkali treatment breaks down lignocellulosic structures by dissolving the lignin (Pellera et al. 2016). It, additionally, increases the buffering capacity of the feedstock, preventing pH drops during acidogenesis (Zhang et al. 2014), providing an advantage over acid treatment for AD. There are limited studies on alkaline pretreatment with a focus on VFA production. For lignocellulosic feedstocks, a solubilization rate of 19% was achieved after alkaline pretreatment but this resulted in more than 40% increase in H_2 production (Ozkan et al. 2011). Guo et al. (2011) achieved a 6 times increase in acetic and butyric acid with NaOH pretreatment, although maximum VFA concentrations were low (<2 g L^{-1}). A study using primary sludge pretreated with different alkali substances found Na_2CO_3 to give a VFA yield 4 times that of untreated sludge. The success was attributed to the increased starting pH (10) which is beneficial for the fermentation and the breakdown of the sludge flocs by the alkali (Lin et al. 2018).

Ozonation uses ozone (O_3) to oxidize, and breakdown, feedstocks and has demonstrated effective delignification of substrates (Travaini et al. 2016; Rosen et al. 2019). Ozone is regarded as safe chemical and environmentally friendly since it quickly decomposes to O_2. The oxidative reactions cause the cell wall of microorganisms to break (oxidative burst), therefore acting as sterilization process (Lone et al. 2019). The disadvantage of ozone treatment is that the high energy demand for ozone production, approximately 12 kWh kg^{-1} O_3 (Gomes et al. 2019; Rosen et al. 2019). For lignocellulosic wastes, hydrogen production was increased by 158% (Yirong et al. 2015), however it negatively affected the dark fermentation of food wastes due to the degradation of proteins and carbohydrates (Yue et al. 2019).

3.2.3 Physical

Thermal treatment accelerates the hydrolysis step by altering the structure of the insoluble fraction, reducing the viscosity and increasing the sCOD. This shifts the AD process towards acidogenesis and inhibits the methanogens (Ariunbaatar et al. 2015), therefore making it suitable for VFA production. A 680% increase in VFA production has been observed after thermal treatment (100 °C, 60 min) for waste activated sludge when the fermentation pH is kept at 9 (Dong et al. 2016). For neutral pH, the increase is slightly lower (~300%). It should be noted that the authors did not mention the pH of the control experiment (untreated), and therefore, they cannot conclude the increase is due solely to pretreatment, as pH adjustment clearly had a significant effect. Lower VFA yield increases (~55%) were observed for food waste (Yin et al. 2014). Thermal treatment in combination with other treatments such as enzymatic treatment or pre-fermentation treatment could increase VFA yields from food waste by 380% (Kim et al. 2005) and 200% (Yu et al. 2016) respectively.

Microwave irradiation combines thermal and non-thermal effects since the electromagnetic field destructs the crystalline structures and heats the aqueous environment simultaneously. This treatment

is highly energy demanding and, therefore, expensive. For the pretreatment of sludge a 66% H_2 increase was observed (Yang and Wang 2017). Microwave irradiation combined with alkaline addition showed a 30% increase in solubilization and a 400% increase in VFA/H_2 production from lignocellulosic waste (Ozkan et al. 2011).

Several investigations suggest that ultrasound (US) is the most efficient physical pretreatment technique (Dhar et al. 2012; Yeneneh et al. 2013; Deepanraj et al. 2017). The ultrasound waves combine physical and chemical substrate degradation by the collapse of cavitational bubbles and the generation of free radicals. US promotes the production of different enzymes or improves the activities of the existing ones, depending on the case. However, its main limitations are high energy consumption and maintenance cost (Cesaro and Belgiorno 2014). US pretreatment improved digestibility of WAS 28 times in terms of sCOD, consequently enhancing acidification (Zhou et al. 2013). US was also tested on food waste, with a disintegration degree of 57% and a maximum VFA production of 0.98 g COD g^{-1} VS (Wu et al. 2015a).

3.2.4 Physiochemical

Thermochemical treatment involves the simultaneous use of a chemical agent and heat. Kumar and Mohan (2018) observed a 4.7 times improvement in the solubilization of vegetable waste using 1% H_2SO_4 and autoclaving at 121 °C for 15 min. This resulted in an AF yield of 0.62 g_{VFA} per g of reducing sugars (under controlled pH 6). However, a comparison of VFA yield between treated and untreated substrate was not provided. Zhang et al. (2017) used diluted HNO_3 for the pretreatment of lignocellulosic waste (corn stover) and concluded that the pretreatment was successful despite only acidifying less than 10% of the soluble sugars.

Ammonia fiber expansion/explosion (AFEX) consist of the use of ammonia, high temperature (60–100 °C) and high pressure (Brodeur et al. 2011), which provokes decrystallization of cellulose (Romero-Cedillo et al. 2017), hemicellulose hydrolysis and disruption of lignin linkage to carbohydrates (Brodeur et al. 2011). Although studies of AFEX pretreated materials for AD/AF are scarce, it has been demonstrated to improve VFA yields by 21% from lignocellulosic substrates (Blasig et al. 1992).

Ionic liquids (ILs) can be used to dissolve cellulose, which can be recovered by addition of water or ethanol; or extract the lignin, making the substrate more biodegradable (Romero-Cedillo et al. 2017). It typically involves heating in temperature ranges of 80–180 °C, therefore this treatment is classified as physiochemical. Pretreatment with ILs for the production of bioethanol from lignocellulosic substrates has been widely explored (Elgharbawy et al. 2016). To the authors knowledge there are no studies of AF using ILs pretreatment. However, some studies focusing on biogas production indicate ILs can improve AD of lignocellulosic substrates, in some cases (Romero-Cedillo et al. 2017). Pretreatment with 1-ethyl, 1-butyl and 1-hexyl-3-methylimidazolium chlorine increased biogas production by 64–140% from different lignocellulosic substrates (Gao et al. 2013). In a study using 1-ethyl-3-methylimidazolium acetate with tomato pomace as substrate, despite the improved enzymatic hydrolysis by cellulase enzymes, pretreated feedstock did not show improved biogas yields. This is presumably due to the formation of inhibitory compounds such as melanoidins and n-derivative amides (Allison et al. 2016). While it can be inferred from AD data that in some cases ILs could improve AF, direct investigation of IL pretreatment for VFA production is recommended.

3.2.5 Biological

Biological pretreatment can be performed with the addition of microorganisms different to AD/AF species, usually fungal, which are better at hydrolyzing the substrate. There have been no studies of fungal pretreatment for AF. Specific extracellular enzymes can also be used, tailored to the feedstock composition. For example, proteases such as trypsin are ideal to hydrolyze protein rich wastes, but this enzyme type can negatively affect acidogenic bacteria, by degrading bacterial proteins (Goldberg 1972; Plácido and Zhang 2018b) and therefore, it is not recommended for VFA production. Consequently, enzymatic pretreatment of variable composition substrates such as OFMSW is often discouraged. Enzymatic pretreatment can be performed in a separate step prior AD/AF or during AD/AF. In the second case, the lifetime of the enzymes can be affected due to the action of endogenous proteases of the AD microorganisms (Odnell et al. 2016). The main advantages of

biological treatments are their non-polluting nature and no waste stream, as the enzymes or biological agent will eventually degrade in AD (Cesaro and Belgiorno 2014; Romero-Cedillo et al. 2017).

3.2.6 Discussion

The discussed pretreatment techniques have demonstrated improved biodegradability of substrates resulting in an increase in VFA or H_2 production, Table 2. Methanogens are more easily affected by toxic compounds than acidogens, therefore if a pretreatment has been discarded for AD it should not be assumed unacceptable for AF.

To enable improvements to the AF process, the pretreatment techniques need to be developed with a specific focus on enhancing VFA production, particularly with novel techniques such as pretreatment with ionic liquids. Alkali/acid treatments are among the most developed chemical pretreatments, with the main disadvantage being toxic compounds generation, however, slight concentrations of toxic compounds might be advantageous to inhibit methanogens. Among the physical techniques, ultrasound looks like the most promising, though it has only been tested on AF of WAS. Biological treatments can be advantageous, as they do not produce toxic compounds like most chemical and physical techniques. Fungi is a cheap viable option to breakdown lignocellulosic feedstock, unfortunately the substrate (organic potential) is also degraded to CO_2 during pretreatment. Extracellular enzymes (microbe-free) have a similar effect but avoiding degradation to unwanted byproducts. However, current commercial enzymes can be expensive. As biological processing and biorefineries develop and become a standard component in the manufacturing landscape, the enzyme market has the potential to expand and offer more affordable options.

Each feedstock presents different challenges in terms of solubilization, thus different pretreatments are recommended. Most of the pretreatment studies of lignocellulosic feedstocks focus on recovering the cellulose and degrading or separating the lignin and hemicellulose. Cellulose is the preferred substrate for bioethanol production, however, AF has the advantage of metabolizing a wider range of substrates including hemicellulose, protein and lipids. Therefore, this aspect should be considered when choosing the pretreatment method. In the case of WAS and microalgae, the challenge resides with the breakdown of the cell walls rather than lignin degradation/removal. Physical pretreatments seem to be the most suitable for this purpose. In the case of food wastes, pretreatment is not a requirement for AD as the long retention time needed for methanogenesis is generally sufficient for the hydrolysis step. However, in the case of VFA production (where shorter HRT are beneficial to inhibit methanogens), pretreatment might be necessary to achieve maximum conversions.

3.3 Fermentation

It is generally accepted by reviewers of AF that most aspects of AF are not well understood (Lee et al. 2014; Kleerebezem et al. 2015; Arslan et al. 2016). These include microbial population of the inoculum; composition of the substrate; as well as fermentation variables (pH, temperature, feeding system, retention times, etc.) and the interactions between them. These factors affect both the product yield and VFAs produced. Majority of experimental studies generate C2–C5 fatty acids therefore this is the focus of this section. The one thing that is agreed upon is that for best AF performance, methanogens need to be inhibited to avoid conversion of VFA to biogas. This can be achieved by addition of inhibitors such as 2-bromoethanosulfophate (Yin et al. 2016) or by operating under unfavorable conditions for methanogens (e.g. $pH < 6$).

3.3.1 AF operating and performance parameters

Comparison of VFA production studies is difficult due to inconsistencies in the definitions and units of key variables reported by different authors. Important operating parameters in AD, such as organic loading rate (OLR), are not often included in the methodology of AF studies. Different feedstocks have different physical properties and composition, therefore reporting OLR in terms of chemical oxygen demand (COD) or volatile solids (VS) allows for a direct comparison between different feedstock types.

VS percentage is commonly used for solid waste and is ideal for characterizing substrate consumption in the context of AD, whereas in AF a smaller percentage of VS will be converted to CO_2 and it is not an indicator of performance as VFAs also account for VS. COD units are better suited to define VFA

concentrations and yields in order to compare values with other soluble materials present in the fermentation broth such as alcohols and monomers released during hydrolysis. The VFA composition is highly dependent on the substrate, therefore standardizing product concentrations in terms of COD allows for comparison across a range of feedstocks. The ratios of each VFA present should also be provided as this will allow for conversion to concentration and an understanding of product distribution.

'Degree of acidification' (DoA) is the amount of soluble COD due to VFA over total soluble COD of the fermented broth (Garcia-Aguirre et al. 2017; Huang et al. 2018). Generally, authors use the term DoA to refer to the VFA yield (Oktem et al. 2006; Alkaya and Demirer 2011; Dahiya et al. 2015; Sarkar and Venkata Mohan 2017). The DoA as defined in this work does not represent the yield of the fermentation, as it does not account for the organic potential of the influent (COD or VS). Instead it is an indicator of the fermentation performance, as it measures the product 'purity' within the aqueous solution. Until significant developments in product recovery and purification are achieved, the fermentation step should aim to reach maximum DoA possible. The most accurate yield definition is mass of VFA produced in terms of COD per total COD fed into the system. Additionally, reporting concentrations is essential as it will highly influence the downstream process, however, it is heavily dependent on the OLR in continuous systems or substrate concentration in batch systems.

Table 3 summarizes each study with the most relevant parameters; hydraulic retention time (HRT), temperature, pH, VFA yield and effluent VFA concentration. In this review, all data has been standardized to the same units to allow for analysis and comparison across the literature available. The parameters were calculated using the data provided by the authors and appropriate unit conversion rates (available as supplementary material).

3.3.2 Reactor mode

The majority of AF research was carried out using bench scale batch reactors (<5 L). Batch fermentations achieved higher VFA concentrations, but this had a negative impact on the yield potentially due to inhibitory VFA concentrations being reached. Maximum VFA concentration achieved from a batch fermentation is 58 g COD_{VFA} L^{-1} using kitchen wastes (Zhang et al. 2005) due to a high substrate concentration (125 g VS L^{-1}). However, the VFA yield was not maximized (< 0.5 g COD_{VFA} g^{-1} VS). Within the same study, a continuous system with solid recirculation (i.e. removal of liquid broth) resulted in a yield increase by 15% compared to batch due to reduced product inhibition (25 g COD_{VFA} L^{-1}). Other studies of continuous fermentations were, typically, carried out using stirred tank type reactors at bench scale. For different substrates it was observed that a minimum of 4 to 5 times HRT was needed to achieve steady state (Maharaj and Elefsiniotis 2001; Lim et al. 2008; Hong et al. 2009). However, instability was observed after 4 to 5 times HRT in some cases (Bengtsson et al. 2008a; Plácido and Zhang 2018b).

Batch studies are useful to provide information on the capability for AF, but for an industrial process they provide limited information as the implications of OLR, solid/liquid recirculation, wash out of methanogens, inoculum adaptation and product removal. To understand the full potential of the VFA fermentation, progression to continuous fermentations is required. The downside to continuous fermentations is they are not as high throughput as batch fermentations, making it difficult to rapidly optimize and gain understanding of the parameter interactions. This is hindered further by every substrate having a different set of optimum parameters. Limited work has been carried out investigating the transition of an optimized batch AF to continuous AF. One example is Yu and Fang (2001) who studied batch and continuous (upflow reactor) AF of dairy wastewaters at different strengths. From the data provided, it can be observed how the product range is significantly different at low strengths (2 g COD L^{-1}): acetic is the predominant acid in continuous (0.27 g COD L^{-1}), and acetic and propionic in batch (0.2 and 0.25 g COD L^{-1} respectively). However, both reactor types behaved similar at high strengths (20 g COD L^{-1}) with propionic as the predominant acid (0.6 g COD L^{-1} in continuous), followed by acetic (0.45 g COD L^{-1}). This similarity is observed in Fig. 4, when comparing OLR to VFA concentration for the data presented in Table 3. The comparable linearity between batch fermentation (g VS L^{-1}) and continuous (g VS L^{-1} day^{-1}) indicates that the results from batch fermentations could, potentially, be used to infer the outcome of a continuous process; although, this needs to be

Table 3 Key operating parameters (reactor type, HRT, OLR, temperature, pH, etc.) and performance data (VFA yield and, VFA concentration) for acidogenic fermentation of organic wastes from different experimental studies

Feedstock	Reactor type	HRT (days)	OLR[1]	T (°C)	pH	Inoculum Type	S/I Ratio	Other conditions
Waste activated sludge	Batch 0.5 L	7	9.9	60	11 (controlled)	Not seeded	N/A	0.02 g Sodium dodecylbenzene sulfonate (SDBS) g^{-1} VS
	Batch 5.0 L	9	12.9	55	8 (controlled)	Not seeded	N/A	–
	Batch 2.0 L	6	10.8	21	6.5 (initial)	Not seeded	N/A	0.02 g SDBS g^{-1} TS
	Batch 2.0 L	6	9.5	21	6.9 (initial)	Not seeded	N/A	0.1 g Sodium dodecyl sulfate (SDS) g^{-1} TS
Primary sludge	Batch 4.0 L	6	10.4	21	6.7 (initial)	Not seeded	N/A	–
	Batch 3.0 L	5	11.6	room	10 (controlled)	Not seeded	N/A	–
	CSTR 3.0 L + clarifier	1.3	2.9	25	6.9 (initial)	Primary sludge	N/A	SRT = 10 days
Food waste	semi-CSTR 2.0 L	8	9	35	6 (controlled)	Digestate	N/A	–
	Batch 0.2 L	9.3	46.1	37	5.5 (initial)	Not seeded	N/A	Ultrasound + acid pretreatment
	Batch 3.0 L	5.0	13.8	35	6.5 (initial)	Digestate	1:1 (v:v)	24 h enzymatic pretreatment with Viscozyme, Flavourzyme and Palatase (1:2:1 at 0.1% v v^{-1})
	Leach bed reactor 3.5 L	14.0	–	50	7 (controlled)	Digestate	96:4 (dry weight)	Leachate recirculation
	Semi-CSTR 4.5 L	11.0	7.1	35	6 (controlled)	Digestate	3:0.8 (v:v)	–
	Batch 2 L	4.0	9.5	35	5.5 (controlled)	Digestate	Not reported	–
	Batch 5 L	3.0	110	–	7 (controlled)	Digestate	20 gVS g^{-1} VS	–
	Semi-CSTR 2.5 L	3.0	10	–	5.5 (controlled)	Mixed digestates from yard w and kitchen/paper waste	N/A	–
	Biofilm reactor 20 L (fed-batch)	2.3	42	30	–	Digestate	N/A	Pre-aeration
	Batch 0.5 L	20.0	60	30	6 (controlled)	Mixed granular sludge and activated sludge	80:20 (dry weight)	–
	Batch 0.35 L	3.0	100	35	7	Digestate	85:15 (wet weight)	–
	Semi-CSTR	7.0	9	40	unfixed	WAS	N/A	–
Protein rich food wastes	Batch 0.5 L	9.0	35	30	6 (controlled)	Granular sludge	5 gVS g^{-1} VS	Tofu, thermal treatment
Kitchen waste	Batch 0.5 L	4	125	35	7 (controlled)	Not seeded	N/A	–
	Semi-CSTR + solid recirculation	3.1	15.52	35	7 (controlled)	Not seeded	N/A	SRT = 9.3 days

Table 3 continued

Feedstock	Reactor type	HRT (days)	OLR[1]	T (°C)	pH	Inoculum Type	S/I Ratio	Other conditions
OFMSW	Batch	4	40	14–22	4–5 (uncontrolled)	Not seeded	N/A	–
	PFR 80 L	4	42	37	6.2 (initial)	Not seeded	N/A	–
	PFR 80 L	6	22.4	55	6.7 (initial)	Thermophilic digestate of urban wastes	N/A	–
Cattail	Batch 2.0 L	5	4.1	40	6.9 (controlled)	Rumen fluid	9:1 (v:v)	Inoculum: rumen fluid
Palm oil mill effluent	CSTR 50 L	4	55	30	6.5 (controlled)	Not seeded	N/A	–
	UASB 12 L	0.9	11.7	35	6 (initial)	Biomass from acidogenic fermenter of dairy wastewater	N/A	–
Olive oil mill effluent	PBBR 2.5 L	1.41	18.3	25	5.5 (initial)	Digestate from olive oil mill effluent	N/A	culture recycling ratio = 0.97
	Batch 0.2 L	40	50	25	6.5 (initial)	Digestate from food waste	10:1 (v:v)	Pretreatment = Solid removal by centrifugation
Wood mill effluent	CSTR 1.6 L + settler	1.5	2	30	5.5 (controlled)	Digestate from brewery industry	N/A	SRT?
	CSTR 1.6 L + settler	1	4.6	30	5.5 (controlled)	Digestate from brewery industry	N/A	SRT?
Paper mill effluent	CSTR 1.0 L	2	27.254	37	5.5 (controlled)	Biomass from acidogenic fermenter	N/A	–
	Batch	12	18.5	room	6 (controlled)	Not seeded	N/A	Ammonia addition (1 g L^{-1})
Cheese whey	CSTR 1.0 L	2	6.5	37	5 (controlled)	Biomass from acidogenic fermenter	N/A	–
Dairy wastewater	Upflow reactor 2.8 L	1.0	2.8	55	5.5 (controlled)	Digestate from dairy wastewater	N/A	P supplement
Gelatin-rich proteinaceous wastewater	Upflow reactor 2.8 L	0.5	2.8	55	5.5 (controlled)	Digestate from dairy wastewater	N/A	–
Slaughterhouse blood	Semi-CSTR 1.0 L	7	19.0	37	7.5 (initial)	Digestate	N/A	–
Pharmaceutical wastewater	CSTR	0.5	9.2	35	5.5 (controlled)	Granular sludge brewery industry	N/A	–
Primary sludge + waste activated sludge	Batch 4.0 L	6	10.4	21	6.7 (initial)	Not seeded	N/A	0.02 g SDBS g^{-1} TS
Primary sludge + starch-rich wastewater	CSTR 3.0 L + clarifier	1.25	3.6	25	6.2 (initial)	Not reported	N/A	SRT = 10 days
Foodwaste + excess sludge	Semi-CSTR 0.5 L	8.9	8.31		7 (controlled)	Digestate	N/A	–
Foodwaste + waste activated sludge	Batch 5.0 L	4	14.4	20	8 (controlled)	Not seeded	N/A	–
Foodwaste + primary sludge	CSTR 5.0 L	5	3.2	room	5.5–5.9 (uncontrolled)	NR	N/A	10% food waste + 90% PS
Sugar industry wastewater + pressed beet pulp	CSTR	2	3.8	35	5.7 (uncontrolled)	Digestate (concentrated)	N/A	1:1 COD mixing ratio, nutrient addition

Table 3 continued

Feedstock	Main acids (% of COD)	VFA yield (mg COD_{VFA} g VS^{-1})	VFA (g COD_{VFA} L^{-1})	VSS reduction	Ref
Waste activated sludge	HAc, HPr (No % reported)	783	7.7	–	Mengmeng et al. (2009)
	45% HAc, 20% HVA	368	4.7	–	Zhang et al. (2009)
	27% HAc, 23% HPr, 20% iHVa	240	2.6	–	Jiang et al. (2007b)
	53% HAc, 12% HPr, 17% iHVa	235	2.2	–	Jiang et al. (2007a)
Primary sludge	32% HAc, 26% HPr, 13% iHBu, 16% iHVa	85	0.9	14.60%	Ji et al. (2010)
	45% HAc, 25% HPr, 13% Hbu, 10% iHVa	302	3.5	38.00%	Wu et al. (2009)
	TVFA reported as HAc	278	1.0	45.80%	Maharaj and Elefsiniotis (2001)
Food waste	49% HAc, 24% HPr, 21% HBu	549	39.5	NR	Lim et al. (2008)
	HAc, Hbu (No % reported)	367	16.9	20%	Elbeshbishy et al. (2011)
	40% HAc, 60% HBu	796	11.0	45%	Kim et al. (2006)
	17% HAc, 9% HPr, 63% HBu	330	49.0	72%	Hussain et al. (2017)
	24% HAc, 13% HPr, 53% HBu	496	39.0	NR	Jiang et al. (2013)
	37% HAc, 16% HPr, 25% HBu	529	5.0	NR	Lim et al. (2000)
	46% HAc, 12% HPr, 42% HBu	265	29.2	NR	Liu et al. (2017)
	40% HAc, 22% HPr, 37% HBu	414	12.4	NR	Pant et al. (2013)
	HAc, HPr (No %)	76	5.3	55%	Sarkar and Venkata Mohan (2017)
	20% HAc, 70% HBu	855	51.3	60%	Wang et al. (2014)
	40% HAc, 40% HBu	443	44.3	NR	Liu et al. (2018b)
	35% HAc, 25% HPr, 15% Hbu	867	54.6	NR	Wu et al. (2015b)
Protein rich food wastes	50% HAc, 25% HBu	613	21.5	61%	Shen et al. (2017)
Kitchen waste	22% HAc, 73% HBu	462	57.8	82%	Zhang et al. (2005)
	HAc, HBu (No % reported)	529	25.5	89%	Zhang et al. (2005)
OFMSW	80% HAc, HPr (No % reported)	35	1.4	NR	Bolzonella et al. (2005)
	76% HAc, 9% HPr, 9% HBu	128	21.4	NR	Sans et al. (1995b)
	23% HAc, 34% HBu, 28% HVa	239	32.1	NR	Sans et al. (1995a)
Cattail	41% HAc, 35% HPr	570	2.3	75.90%	Hu et al. (2006)
Palm oil mill effluent	41% HAc, 30% HPr, 29% HVa	368	20.3	63%	Rahmani et al. (2015)
	41% HAc, 59% HPr	490	5.2	NR	Borja et al. (1996)
Olive oil mill effluent	62% HAc, 22% HBu	414	10.7	NR	Beccari et al. (2009)
	54% HAc, 37% HBu	312	15.6	–	Dionisi et al. (2005)
Wood mill effluent	51% HAc, 39% HPr	464	1.4	NR	Ben et al. (2011)
	62% HAc, 32% HPr	437	2.0	NR	Mato et al. (2010)
Paper mill effluent	24% HAc, 48% HBu	96	5.3	NR	Bengtsson et al. (2008a)
	HAc, HBu (No % reported)	798	14.8	NR	Jiang et al. (2012)

Table 3 continued

Feedstock	Main acids (% of COD)	VFA yield (mg COD_{VFA} g VS^{-1})	VFA (g COD_{VFA} L^{-1})	VSS reduction	Ref
Cheese whey	HAc, Hbu (No % reported)	367	4.8	NR	Bengtsson et al. (2008a)
Dairy wastewater	33% HAc, 22% HPr, 17% Hbu	453	1.3	NR	Yu and Fang (2000)
Gelatin-rich proteinaceous wastewater	14% HAc, 14% HPr, 15% iHBu, 17% HBu, 12% iHVa, 17% HVa	1568	2.2	NR	Yu and Fang (2003)
Slaughterhouse blood	21% HAc, 35% Hbu, 27% iHVa	967	128.6	NR	Plácido and Zhang (2018b)
Pharmaceutical wastewater	50% HAc, 19% HPr, 32% Hbu	794	3.6	NR	Oktem et al. (2006)
Primary sludge + waste activated sludge	21% HAc, 29% HPr, 14% iHVa	174	1.8	23.60%	Ji et al. (2010)
Primary sludge + starch-rich wastewater	HAc, HBu (No % reported)	289	1.3	74.60%	Maharaj and Elefsiniotis (2001)
Foodwaste + excess sludge	Not reported	393	29.1	NR	(Hong and Haiyun 2010)
Foodwaste + waste activated sludge	32% HAc, 52% HPr	576	8.3	61.00%	(Feng et al. 2011)
Foodwaste + primary sludge	48% HPr, 52% HBu	148	2.4	NR	(Min et al. 2005)
Sugar industry wastewater + pressed beet pulp	40% HAc, 51% HPr	511	3.9	NR	(Alkaya and Demirer 2011)

[1]OLR (batch: g L^{-1}; continuous: g VS L^{-1} day^{-1})

NR: Not reported

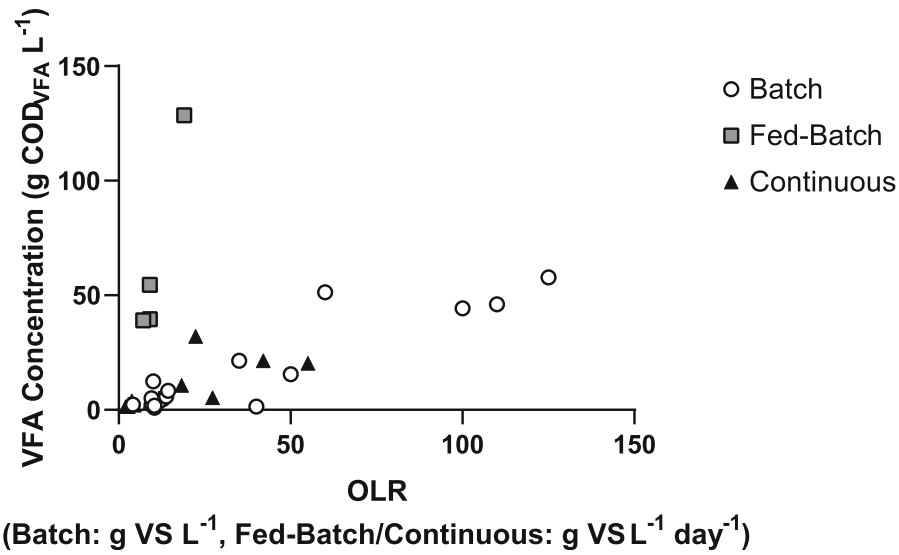

Fig. 4 Impact of OLR on VFA concentration depending on reactor operating mode, from collated literature data in Table 3. White circle batch; Black square fed-batch; Black up-pointing triangle continuous

experimentally validated. In contrast, fed-batch fermentations do not follow the same response. The higher VFA concentrations in fed-batch AF is expected due to the additional available substrate, compared to batch or continuous (where some unfermented substrate will be removed in the outlet stream). Interestingly, these results have not plateaued out in terms of VFA concentration, meaning that the expected VFA toxicity at high concentrations has not been confirmed by this data. This indicates that the fermentation system can be pushed towards higher VFA concentrations, which will improve the downstream processing. To aid the rate of development, it would be beneficial to understand how the transition from batch to continuous processing impacts the fermentation parameters.

3.3.3 Inoculum and microbial community

In AF processes, VFA yield and distribution, for a given substrate, are in essence a result of the microbial community and its activity. Microbial community studies can help understand the acidogenic fermentation process and the effect of fermentation conditions. A wide range of microbes contribute to the fermentation, and further research is necessary to associate each microbe type to their specific or main role within AF. Taxonomic identification of communities is typically carried out by 16S rDNA gene sequencing analysis with results shown in terms of relative abundance (Atasoy et al. 2019).

Acidogenic species can be introduced by an inoculum/seed and the substrate or the substrate alone, Table 3. Most AF studies use AD digestate/sludge as the inoculum due to the presence of more acidogens compared to other inoculums such as aerobic activated sludge (Wang et al. 2014; Yin et al. 2016). However, AD sludge contains methanogens which degrade the VFA. In batch fermentations, optimizing the substrate to inoculum ratio (S/I in g VS g^{-1} VS) can help inhibit methanogens (Guo et al. 2014). A S/I higher than 3–4 is found to inhibit methanogens successfully (Alzate et al. 2012; Guo et al. 2014). Inoculum acclimation can be another strategy to improve batch AF. Plácido and Zhang (2018b) observed a 43% increase in VFA when inoculum was acclimated by operating a continuous reactor for at least three times HRT. Some authors suggest subjecting the inoculum to a thermal treatment to inhibit methanogens. However, there is little information on optimal conditions to carry out this heat shock treatment (Wainaina et al. 2019) and the effect it has on AF. Often, the conditions used seem arbitrary or based on H_2 production (Tampio et al. 2018; Jayakrishnan et al. 2019). 2-bromoethanesulfonate (BES) is commonly used to inhibit methanogens, but its effect on acidogens is not well understood. Yin et al. (2016) found that addition of BES was effective in inhibiting methanogens and had no significant effect on VFA distribution, however, it affected the relative abundance of microbes.

In acidogenic fermentation, microbes (generally bacteria) carry out biological conversion of

macromolecules e.g. protein, carbohydrate and lipids, to VFA and by-products via their metabolic activities. Anaerobic sludge derived from wastewater treatment mostly contains phyla belonging to *Firmicutes*, *Proteobacteria*, *Bacteroidetes*, *Actinobacteria, Chloroflexi* and *Euryarchaeota* (Li et al. 2019; Greses et al. 2020). *Euryarchaeota* phylum encompass methanogens. High abundance of *Firmicutes* is associated with high acidification yields due to their hydrolytic and acidogenic capabilities (Yin et al. 2016; Atasoy et al. 2019; Greses et al. 2020), particularly *Clostridium* genus (Atasoy et al. 2019). *Firmicutes* proliferate when substrate has high carbohydrate content (Iglesias-Iglesias et al. 2019; Greses et al. 2020). The genus with highest number of genes related to amino acid and carbohydrates metabolism are *Pseudomonas* (*Proteobacteria*) and *Clostridium* respectively (Iglesias-Iglesias et al. 2019).

AD sludge with similar microbial composition can be in slurry or granular form, and these physical properties can influence AF performance. AF using large granular sludge ($\sim$3.5 mm) resulted in higher DoA and yields from glucose at pH 10 compared to typical slurry form (Atasoy et al. 2019). Large granules were also more effective in AF of cheese industry wastewater (Atasoy et al. 2020). Despite the differences in microbial relative abundance after 5 days of fermentation, the type of sludge did not significantly affect the VFA distribution, suggesting that pH and fermentation conditions have a larger influence over final product distribution (Atasoy et al. 2019). Differences in microbial relative abundance were observed with the same inoculum when either milk or cheese industry wastewater were used, indicating that relative abundance also depends on substrate type (Atasoy et al. 2020). The same observations have been made for AD and biogas processes (Kushkevych et al. 2019), indicating that a period of adaptation for the microorganisms to adjust to the feedstock is likely to be required before stable operation is achieved.

The inoculum will determine the type of microbes introduced in the system, but the relative abundance can be modified by fermentation conditions and substrate type. Just like VFA distribution, fermentation pH and temperature affect microbial relative abundance. In AF of food waste under mesophilic conditions, neutral pH and pH 5 led to high abundance of classes *Clostridia* (>50%) and *Bacilli* (>50%) respectively. At neutral pH, thermophilic conditions increased the relative abundance of *Bacteroidia* compared to mesophilic conditions. At pH 5 the change in relative abundance due to temperature was less significant (Zhang et al. 2020). At mesophilic conditions, pH changes also had significant effect on microbial relative abundance of potato waste fermentation (Li et al. 2019); at pH 6 the major phyla were *Proteobacteria* and *Firmicutes*, whereas at pH 7 and 8 (highest VFA yields), *Bacteroidetes* and *Firmicutes* dominated. The highest *Euryarchaeota* (methanogens) relative abundance was observed at pH 7 (Li et al. 2019). When using sewage sludge as substrate: pH 7–8 resulted in high levels of *Euryarchaeota* (60%) and *Firmicutes* (20%), followed by *Actinobacteria*. These results suggest that, if operating at neutral pH methanogenic inhibition strategies are required for optimum AF (e.g. BES addition or inoculum pretreatment). At pH 9 (highest VFA yield) dominating phyla were *Firmicutes* (60%, mostly *Clostridia*) and *Actinobacteria* (24%). pH 10 led to 35% *Firmicutes*, 39% *Actinobacteria* and 16% *Proteobacteria* (Chen et al. 2017).

It has also been found that different substrates influence the relative abundance, especially at a genus level. Majority of phyla found in AF of food waste (Yin et al. 2016; Zhang et al. 2020) and sewage sludge (Iglesias-Iglesias et al. 2019) belongs to phyla *Firmicutes*, *Proteobacteria* and *Bacteroidetes*. Under limited aeration (non-strict anaerobic), the two major classes in food waste AF at pH 6 is *Clostridia* (Yin et al. 2016; Zhang et al. 2020) and *Bacilli* at pH 5 (Zhang et al. 2020). Under strict anaerobic conditions classes *Bacteroidia* (phylum *Bacteroidetes*) followed by *Gammaproteobacteria* (phylum *Proteobacteria*) tend to dominate the community (Yin et al. 2016). The presence of BES negatively affects *Proteobacteria*, reducing the relative abundance to insignificant levels (Yin et al. 2016). Greses et al. (2020) investigated cucumber, tomato and lettuce as substrates, all three substrates led to high levels of class *Clostridiales*, but *Ruminicocus* were only significant in cucumber and tomato fermentations. AF of lettuce resulted in significant levels of *Acidaminococcus.* In contrast with food waste, for AF of sewage sludge (non-strict anaerobic), the most abundant phyla were, *Proteobacteria* followed by *Bacteroidetes* and *Firmicutes* (Iglesias-Iglesias et al. 2019). *Proteobacteria*

is mostly represented by *Alphaproteobacteria*, *Betaproteobacteria* and *Gammaproteobacterial* (Iglesias-Iglesias et al. 2019). Apart from pH, temperature and substrate composition, strong correlations between the microbial consortia with organic loading rates, and oxidation–reduction potential, were found (Xin et al. 2018).

Genomic studies allow the quantification of microbial diversity. Microbial diversity, particularly for complex substrates such as food waste, is strongly linked to high VFA yields (Zhang et al. 2020) and performance stability (Xin et al. 2018). Introducing extra substrates (co-fermentation) can improve microbial diversity and consequently improve VFA yields. Xin et al. (2018) demonstrated that by introducing pretreated corn stalk and pig manure as co-substrates to AF of pretreated WAS, microbial diversity improved and VFA yield of AF of the three substrates was almost two fold that of pretreated WAS alone (based on initial soluble COD and maximum VFA concentration (in COD units)).

While mixed cultures are beneficial to metabolize complex substrates, it is likely to result in multiple product solution with fewer applications. Recent research has focused on how to optimize the inoculum and culture to target a single product through bioaugmentation techniques. One approach is to mix different mixed culture inocula to optimize the process for a targeted product and substrate (Ai et al. 2013). A more rigorous approach was taken by Atasoy and Cetecioglu (2020) who studied the bioaugmentation of mixed culture with the introduction of *Clostridium butyricum* monoculture to target butyric acid production from cheese industry wastewater in a sequencing batch reactor. This is achieved by injecting a small percentage of the reactor volume with the aseptically grown target culture. The bioaugmented reactor saw a 4.6 and 2.3 times increase in HBu and total VFA average yield, respectively, compared to the control reactor, resulting in an increase of HBu selectivity from 21 to 61% (Atasoy and Cetecioglu 2020). Results also show improvement with respect to the monoculture fermentation, indicating syntrophic relationships between the mixed culture and *Clostridium butyricum*. Bioaugmentation also helped with overall production stability (Atasoy and Cetecioglu 2020).

3.3.4 pH

In AF, pH is a key parameter to control VFA yields and product distribution, controlled by acid/base addition. Optimum pH for methanogens is 7.0. Acidogenic bacteria can handle wider pH ranges, therefore pH has a relevant role in AF to minimize VFA degradation. A slightly acidic pH (5–6) improves hydrolysis due to higher hydrolytic bacteria activity (Jiang et al. 2013), and inhibits methanogens, but pH lower than 5 is inhibitory for acidogens (Bengtsson et al. 2008a; Wang et al. 2014). This is due to the high toxicity of VFA in their free acid form, which is more dominant when the pH is less than the pKa (Table 1) (Arslan et al. 2016). The toxic effect could be overcome with continuous in situ product recovery. Alkaline pH (8–10) can also be beneficial (Feng et al. 2011) as it improves substrate digestibility by dissolving lignin (abiotic effect), inhibits methanogens and it offers buffering capacity (Zhang et al. 2009). At pH 11 or higher, the metabolic activity of acidogens slow down due to the toxic effects of strong alkaline conditions (Mengmeng et al. 2009). Alkaline addition can substantially add to operational costs. In contrast, acidic pH can be achieved by accumulation of VFA, depending on the buffering capacity of the fermentation broth. As a general rule, alkaline pH will favor acetic acid production, while acidic pH will favor propionic and butyric acids (Zhang et al. 2009; Wu et al. 2009; Garcia-Aguirre et al. 2017). In some cases, neutral pH (7) showed better VFA yields. For example, gelatin degradation efficiency was 98% at neutral pH compared to 85% at pH 5, resulting in higher VFA concentrations (Yu and Fang 2003). In the case of kitchen wastes, pH 7 also had the highest solubilization rate of 82% in terms of COD, which coincides with highest VFA concentration, compared to less than 70% for acidic or alkaline pH (Zhang et al. 2005). This could be explained by the differences in substrate composition, as hydrolysis of proteins and lipids is optimum at neutral pH (Arslan et al. 2016). These results indicate that the pH has a greater impact on the hydrolysis step, which is widely acknowledged as the second rate limiting step in AD. This further supports that the optimum pH is going to be substrate dependent.

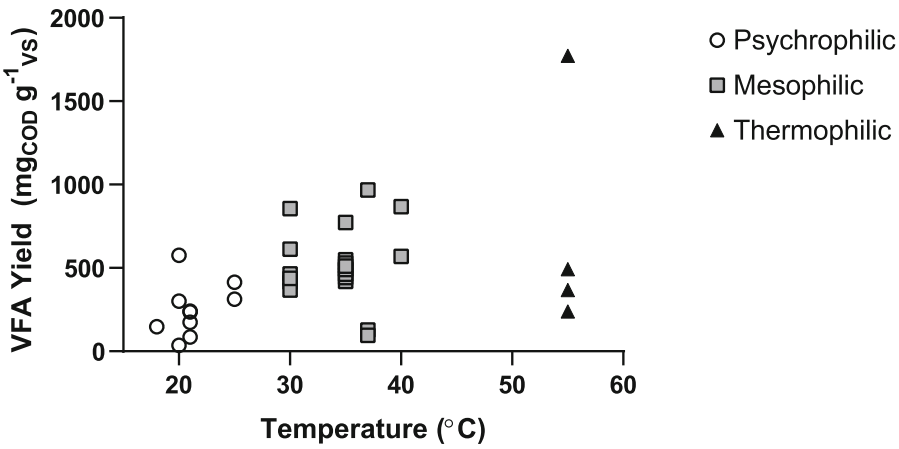

Fig. 5 Impact of AF temperature on VFA yield, from collated literature data in Table 3. White circle psychrophilic; Black square mesophilic; Black up-pointing triangle thermophilic

3.3.5 Temperature

Temperature has a significant effect on yield and the type of VFA produced. Typically, fermentations can be classified by operating temperature, as either psychrophilic (<25 °C), mesophilic (25–45 °C) or thermophilic (>45 °C). Generally, under thermophilic conditions VFA accumulation is higher compared to mesophilic conditions (Yu and Fang 2003; Zhang et al. 2009; Garcia-Aguirre et al. 2017). Thermophilic temperatures can improve the hydrolysis of solid wastes improving overall digestibility, but pH has a greater influence over this compared to temperature (Garcia-Aguirre et al. 2017). Kinetics under thermophilic conditions, however, are slow therefore longer retention times are required to reach maximum product concentrations (Zhang et al. 2009; Garcia-Aguirre et al. 2017). It should be considered that the higher temperature leads to higher operating costs. Higher VFA yields are achieved at mesophilic temperatures, Fig. 5. This indicates there is a better conversion for substrate to product, although the lower VFA concentrations will be less favorable for product recovery. VFA production at psychrophilic temperatures (~10 °C) is feasible but not competitive with mesophilic production (Maharaj and Elefsiniotis 2001), Fig. 5, with lower VFA concentrations and yields achieved.

Temperature has the potential to influence type of VFA produced, but the current results are inconsistent (Zhang et al. 2009); this is probably due to the lack of knowledge on parameters interactions. For example, temperature can have an effect on ammonia release (Jiang et al. 2013) making it difficult to study the independent effect of these variables. Garcia-Aguirre et al. (2017) found that temperature had no significant effect on product distribution for slaughterhouse wastewater and paper mill wastewater, with the same observation was made for protein rich wastewater (Yu and Fang 2003). However, for OFMSW and winery wastewater, butyric acid was predominant (>70% of COD) at acidic pH (5.5) and thermophilic temperature, compared to propionic and acetic predominance under any other conditions (Garcia-Aguirre et al. 2017). This is further supported by Jiang et al. (2013) who also found that thermophilic temperatures promote butyric acid production from food waste at pH 6 (Jiang et al. 2013).

3.3.6 Organic loading rate and substrate concentration

The organic loading rate (OLR) is the amount of organic material fed (in VS) per volumetric unit of the reactor per unit of time. The recommended values for AD range from 2 to 7 g VS L^{-1} day^{-1} (Hobson and Wheatley 1994; Gerardi 2003). Using higher values of OLR can help stop methane production and promote acidogenesis. Increasing OLR above the AD threshold (7 g VS L^{-1} day^{-1}) results in higher VFA concentrations but lower yields (Lim et al. 2000; Jiang et al. 2013; Liu et al. 2018b). Ideally, a compromise between the yield and the VFA concentration should be found. Dry substrates (TS ~ 20%) are preferred to slow down methanogen kinetics and maximize VFA production, although VS destruction is lower (Liotta et al. 2014).

3.3.7 Hydraulic retention time

HRT plays an important role in AF. Short HRTs (<10 days) are preferred to wash out the slower growing methanogenic microorganisms (Hobson and Wheatley 1994; Gerardi 2003). However, if the substrate is a solid waste, short retention times will result in lower yields as hydrolysis is, generally, the rate limiting step (Fdez.-Güelfo et al. 2011). Pant et al. (2013) found that to achieve maximum conversion in the fermentation step at least 3 days HRT is required. In batch mode, maximum VFA concentrations are typically achieved in 4–9 days, indicating relatively short retention times are needed.

3.3.8 Feedstock

The type of feedstock will affect the output of the fermentation. Comparison on feedstock compositions is difficult due to differences in AF parameters used. Feedstock compositions for the same type can also vary depending on location or season, for example, resulting in high variability in the reported data. There are numerous studies available to compare AD performance for different feedstock types (Chynoweth et al. 1993). Similar studies on AF towards VFA production are scarce. Although AD studies can serve as reference, optimum substrate compositions might be different for AF. Cheese whey, molasses and OFMSW showed higher VFA potentials over wastes such as glycerol, slurry, winery wastewater, olive mill effluent and landfill leachate (Silva et al. 2013). This was further supported by Garcia-Aguirre et al. (2017) who indicate that OFMSW has the highest VFA potential compared to slaughterhouse wastewater, paper mill wastewater, winery wastewater, crude glycerol, sewage sludge, and meat and bone meal. Further investigation is necessary to obtain optimum substrate composition ranges for AF.

The feedstock composition can be modified by mixing different substrates, in which case the process is known as co-digestion or co-fermentation. Co-fed substrates are known to improve yields due to synergistic effects (Feng et al. 2011). It can also help dilute toxic compounds present in the feedstocks and improve nutrients ratio, e.g. adding protein substrates improves N content. Hong and Haiyun optimized the co-fermentation of food waste and excess sludge, obtaining maximum VFA concentration of 29 g L^{-1} for 88% (VSS basis) food waste (Hong and Haiyun 2010). The synthetic food waste used in this study did not contain animal products, indicating that a certain amount of protein derived from the excess sludge was beneficial. In a different study using WAS, potato peel waste and food waste, it was found that carbon-rich substrates promoted butyrate production, whereas more proteinaceous feedstocks led towards propionate and valerate, with acetate being the predominant VFA in all cases (Ma et al. 2017). The highest VFA yield observed in this study, 344 mg COD g^{-1} VS, corresponded to a ratio of WAS to potato peel of 1:3 (in terms of VS).

Using the data presented in Table 3, a principal component analysis (PCA) was performed to elicit a more comprehensive assessment of the current literature considering both AF operating parameters and fermentation performance. The analysis only used references where data for all variables investigated was present. The first four PCs can collectively explain 72.5% of the variability in the data. The data set used for this analysis is available (Outram and Ramos Suarez 2020).

Feedstock has to be treated as a qualitative parameter. If a breakdown of feedstock components was often provided, either elemental or more simplified such as carbohydrate, protein, fat etc. then this could be added to the analysis as a quantitative variable; although this would need to be consistently reported across all literature. The feedstock's in Table 3 were simplified into six main categories, sludge, food waste (including MSW), high protein, industrial, lignocellulosic and co-fed, i.e. mixed feedstocks. Assessment of the PC plots demonstrated clustering based on feedstock type, with similar patterns occurring between similar feedstock types e.g. food waste and high protein or sludge and co-fed (which in most cases partially consisted of sludge), Fig. 6.

The clustering is evident when considering the VFA concentration, Fig. 7. High protein wastes, including food waste, produce a higher VFA concentration and yield than other feedstock types. They have the potential to release high concentrations of ammonia, which can inhibit organisms that degrade VFAs, therefore a build-up of VFAs is observed (Plácido and Zhang 2018b). This analysis demonstrates that some feedstock types are more suited to VFA production than others.

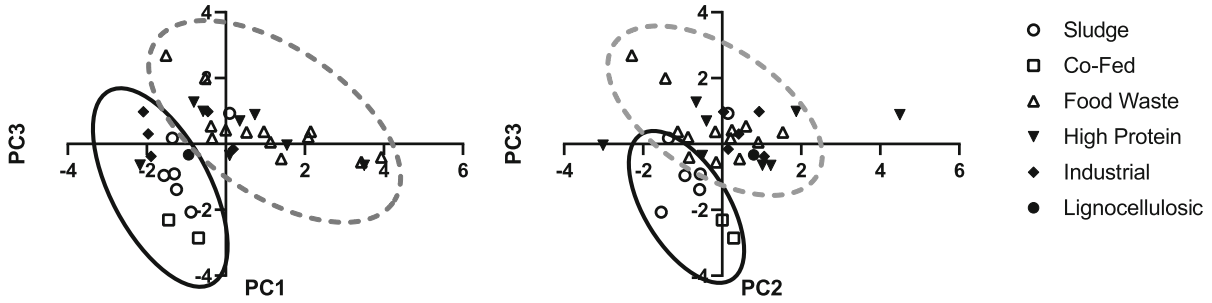

Fig. 6 PC scores plots categorized by feedstock type, with clustering based on similar feedstock types circled (solid line sludge/industrial waste, dashed line high protein/food waste). White circle sludge; White square co-fed; White up-pointing triangle food waste; Black down-pointing triangle high protein; Black diamond suite industrial; Black circle lignocellulosic

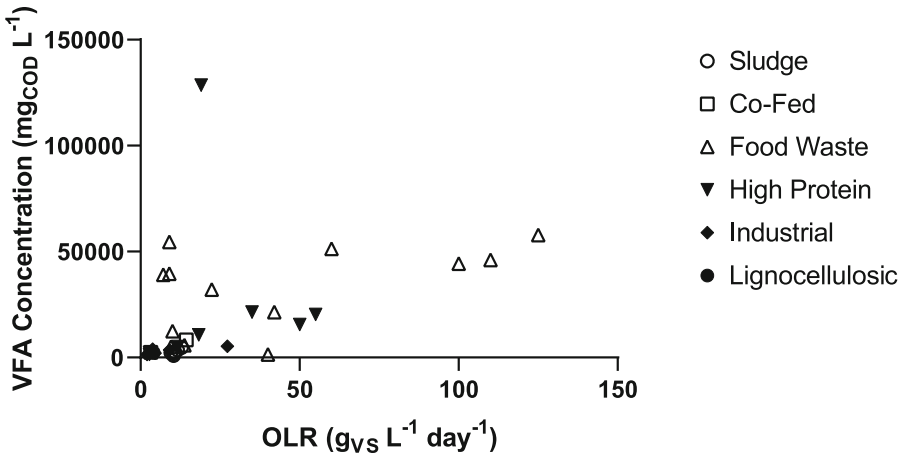

Fig. 7 OLR vs VFA concentration with respect to feedstock classification. White circle sludge; White square co-fed; White up-pointing triangle food waste; Black down-pointing triangle high protein; Black diamond suite industrial; Black circle lignocellulosic

When considering the impact of each variable on the individual PCs, Fig. 8, it can be observed that all three PCs have a high dependency on a single acid concentration. Therefore, the acid percentage distribution by feedstock type was considered, Fig. 9. In the majority of fermentations acetic acid was the main, or second, most abundant acid, hence most of the data points are in the bottom left quadrant in Fig. 9. Sludge-based AF produced mainly HAc, with a small proportion of HPr. In comparison, high protein and food waste feedstock's produced more HBu than HPr. Industrial wastes, such as wood mill effluent, and lignocellulosic feedstocks had a tendency towards HPr production. This demonstrates the feedstock influences the final product composition.

3.3.9 Developing AF

The knowledge gained in AF parameters is highly dependent on feedstock type. Food waste is the most widely studied feedstock, followed by primary and waste activated sludges. The optimum parameters of AF towards VFA production for each substrate have not been established. Although the production of microbial VFA has proven feasible, the process is not as well understood especially compared to AD. To move forward, more optimization studies using both batch and continuous systems are necessary. As main variables are not independent, Arslan et al. (2013), and Hong and Haiyun (2010) suggest the use of statistical design of experiments (DoE) to optimize the VFA production and to understand the parameters interactions and influence.

Additionally, VFAs are inhibitory compounds, although inhibitory concentrations are generally

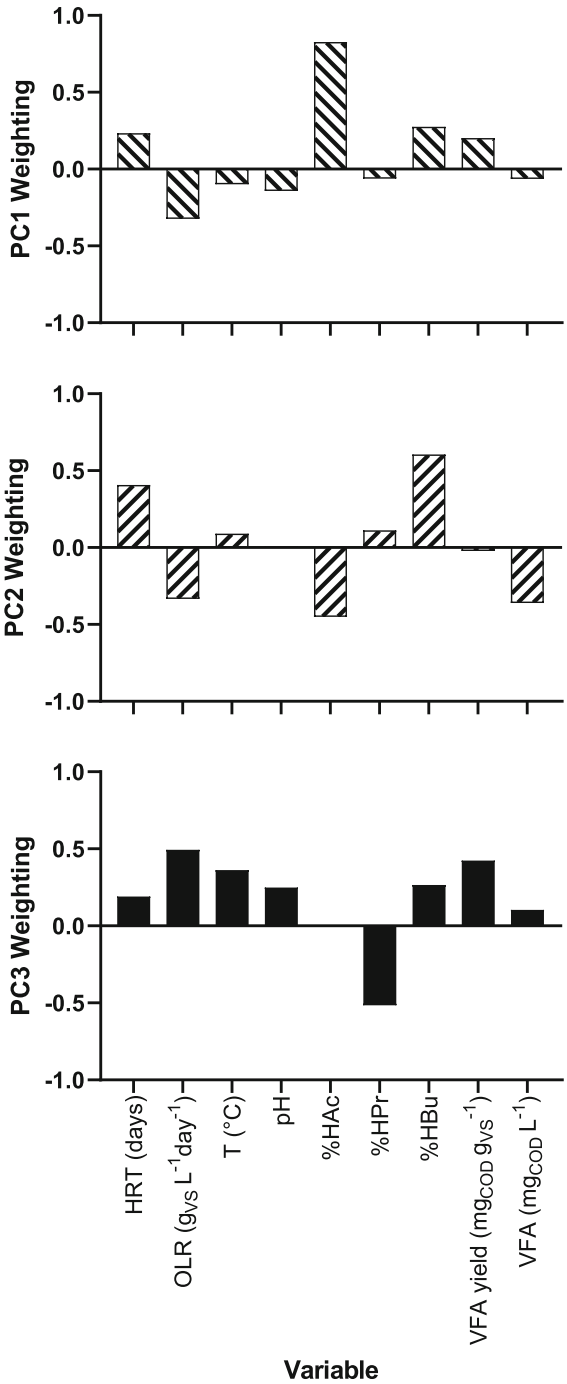

Fig. 8 Weighting of each variable on individual principal components. Top: PC1, middle: PC2, bottom: PC3

reported towards hydrogen and methane production, with propionate being the most toxic. In pure-culture acidogenic fermentations, propionate can be inhibitory at low concentrations of 10 g L^{-1} (Bhatia and Yang 2017). Veeken et al. (2000) found that at 30 g_{VFA} COD L^{-1} and pH 5 inhibits the hydrolysis rate. Establishing the exact VFA concentration thresholds is difficult as it depends on operational variables, microorganism consortium and type of VFA produced. A better understanding in this topic, could help establish the maximum potential of AF without the aid of in situ product recovery (ISPR).

3.4 Primary recovery of VFAs from AF

Due to product toxicity and possible product degradation, recovery of VFAs from the AF is of strategic importance. Lopez-Garon and Straathof (2014) have provided a detailed review on the recovery of single carboxylic acids from pure culture fermentations. Whilst the overall processing steps are likely to be similar, mixed VFA recovery is more complicated due to the mixture of acids that need to be separated if they are to be sold as chemicals. Before a separation process is chosen, the final product use of the VFA should be considered as this will influence the downstream processing. Based on the current literature, this is generally not taken into consideration. The recovery process must selectively target the VFAs over other fermentation broth components including water, and increase their concentration in the product stream (Reyhanitash et al. 2017). The energy demand, and the number of unit operations required to achieve the desired product stream, and the fermentation broth conditions should be considered when designing the recovery process.

The properties of the fermentation broth play a key role in designing a product recovery process. AF broths will generally contain suspended solids including cells; VFAs and other soluble compounds. VFAs are extracellular products and, therefore, can be found in the liquid fraction without the need for cell disruption. Many studies achieved VFA concentrations of 10–60 g COD L^{-1}, Table 3. To facilitate product recovery, higher VFA concentrations are most desirable. Most AF studies were carried out at neutral or slightly acidic pH. The concentration and composition of soluble compounds is highly dependent on the substrate used, chemical addition to control pH, and the fermentation performance in terms of by-products formation. Suspended solids are generally at high concentrations when solid wastes are used as substrate. VSS from AF of primary sludge varied

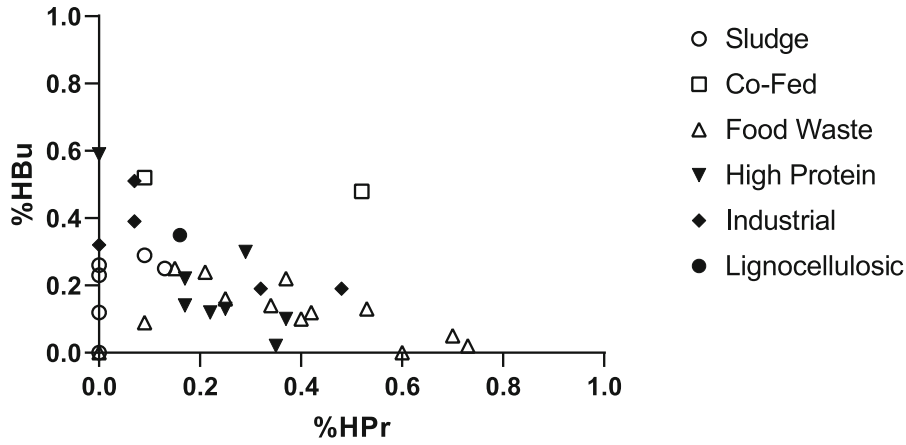

Fig. 9 Comparison of the ratio of propionic and butyric acid produced with respect to feedstock classification. White circle sludge; White square co-fed; White up-pointing triangle food waste; Black down-pointing triangle high protein; Black diamond suite industrial; Black circle lignocellulosic

between 6 and 9 g L^{-1}, depending on fermentation conditions (Wu et al. 2009). Properties of the fermentation broth excluding VFA concentrations are often unreported with very few exceptions. 200 mg NH_4^+–N L^{-1} was reported in AF broth from WAS (Mengmeng et al. 2009). Nitrogen and phosphorus concentrations fell in the ranges of 50–300 mg NH_4^+–N L^{-1} and 20–50 mg PO_4^{3-}-P L^{-1} respectively. 100–2000 mg NH_4^+–N L^{-1} and were observed in broths from food waste and kitchen wastes (Zhang et al. 2005; Jiang et al. 2013; Wang et al. 2014). As these concentrations are low, they have low probability of affecting the recovery process. Other ions such as Na^+, which are present as a result of NaOH addition for pH regulation, are more likely to have an impact as they can be found at concentrations of up to 25 g L^{-1} (Zhang et al. 2005).

This section discusses all the recovery techniques that have been researched with regards to mixed VFA production from AF. The focus is on the primary separation integrated with the fermentation step for ISPR to relieve product inhibition and enable a continuous fermentation for improved VFA yields. The key factors for recovery selection and integration for each technique are collated in Table 4.

3.4.1 Adsorption

Adsorption is a common technique used for product recovery from bioprocesses. It relies on the formation of a bond between the target compound and a selective adsorption resin. A desorption step is required to recover the VFA and regenerate the adsorbent for further use.

Cabrera-Rodríguez et al. (2017a), Rebecchi et al. (2016), Reyhanitash et al. (2017) and Yousuf et al. (2016) all investigated adsorption of VFA from mixed culture fermentations. Unlike other product recovery techniques, there is no consensus over the mechanism of separation and pH conditions for optimal recovery, as this is dependent on the adsorbent used. Resins bind with the acids via ion exchange, when the acids are in the dissociated form (pH > pKa), or hydrophobic interactions when in the free acid form (pH < pKa) (Cabrera-Rodríguez et al. 2017a). This increases the flexibility of integrating adsorption with AF, as an appropriate adsorbent can be selected depending on fermentation conditions. All adsorption investigations focused on amine-based anion exchange resins. The use of an amine as a conjugation ion is similar to liquid–liquid extraction, where amine-based extractants (e.g. trioctylamine) are used for carboxylic acid recovery (Kertes et al. 2009). Rebecchi et al. (2016) found that the Amberlyst A21 (tertiary amine) had the best adsorption performance (based on adsorption yield and solid phase VFA concentration) in grape pomace digestate, although an adsorption yield of only 11% was achieved. Amberlyst A21 being 3.5–47 times cheaper than the other resins tested also helped its favorability (Rebecchi et al. 2016). Reyhanitash et al. (2017) found the non-functionalized resin (Lewatit VP OC 1064 MD PH) to have the highest VFA adsorbing capacities, relying on the hydrophobic interactions. The more hydrophobic the VFA, the higher selectivity with the adsorbent was observed. This higher capacity could also be related to the non-functional resin not adsorbing mineral acids formed in the fermentation broth, unlike with the functionalized resins

Table 4 Overview of reported VFA recovery techniques and the key requirements for successful separation

Technique	Separation mechanism	pH requirement	Selectivity[a]	Recovery pretreatment performed	Recovered VFA form	Other broth components removed?	References
Adsorption	Electrostatic/ affinity	pH > pKa[b]	HBu > HAc	Clarification (typically centrifugation followed by ultrafiltration at 0.2 μm)	Depends on desorption step	Other anions	(Yousuf et al. 2016; Rebecchi et al. 2016; Cabrera-Rodríguez et al. 2017a; Reyhanitash et al. 2017)
Distillation	Evaporation	–	HBu > HAc	Biomass removal	$Acid_{(aq)}$	Unreported	(Mumtaz et al. 2008)
Electrocoagulation	Electrostatic	pH > pKa[c]	HAc > HBu	None	$Acid\ salt_{(aq)}$	Yes[d]	(Fayad et al. 2017)
Electrodialysis	Electrostatic	pH > pKa[c]	HAc > HBu	Clarification	$Acid\ salt_{(aq)}$ (e.g. CH_3COONa)	Other anions	(Jones et al. 2015, 2017; Zhang and Angelidaki 2015; Scoma et al. 2016; Tao et al. 2016; Arslan et al. 2017; Domingos et al. 2018; Pan et al. 2018)
Esterification	Reactive	pH < pKa[e]	HVa > HAc	Clarification	Ester	Unreported	(Plácido and Zhang 2018a)
Filtration	Size	Neutral[f]	n/a	Clarification	$Acid_{(aq)}$	High possibility, unreported	(Zacharof and Lovitt 2014; Longo et al. 2015; Jung et al. 2015; Xiong et al. 2015; Trad et al. 2015; Zacharof et al. 2016)
Freeze/Thaw	Physical	Fermentation	None	None[g]	$Acid_{(aq)}$	Yes[g]	(Omar et al. 2009)
Gas stripping	Evaporation	pH < pKa	HBu > HAc	None	Acid salt	Unreported	(Li et al. 2015)
Liquid–liquid extraction	Affinity/ Reactive	pH < pKa	HBu > HAc	Clarification	$Acid\ complex_{(org)}$	Other anions	(Mostafa 1999; Alkaya et al. 2009; Reyhanitash et al. 2016; Bekatorou et al. 2016; Rocha et al. 2017)
Membrane extraction	Affinity/ Reactive	pH < pKa	HBu > HAc	Solid removal (e.g. coarse (1–2 mm) filtration)	Extractant dependent	Unreported, high possibility (extractant dependent)	(Yesil et al. 2014; Tugtas 2014; Aydin et al. 2018; Plácido and Zhang 2018a; Outram and Zhang 2018; Dessì et al. 2020)
Pervaporation	Affinity/ evaporation	pH < pKa	HBu > HAc	Clarification	$Acid_{(aq)}$	Unreported	(Choudhari et al. 2015; Yesil et al. 2018)
Salting-out (extraction)	Affinity	pH < pKa	HBu > HAc	Clarification	$Acid_{(org)}$	Unreported	(Fu et al. 2015, 2017)

[a]Selectivity focuses on two main acids produced in Table 3, generally if HBu > HAc then selective towards longer chain VFAs and vice versa

[b]Generally, although if separation is primarily affinity based then pH < pKa is required (Yousuf et al. 2016)

[c]Needed in salt form, separation hindered if pH is too high

[d]Electrocoagulation removes solids from broth with VFA remaining, likely that other soluble components remain with VFA

[e]H_2SO_4 used as acid catalyst (Plácido and Zhang 2018a)

[f]Depends on membrane and desired process operation – Xiong et al. (Xiong et al. 2015) required pH 3 whereas Jung et al. (Jung et al. 2015) used pH 8

[g]Freeze/thaw is a method to remove suspended solids from the fermentation broth, with a concentrating effect

(Reyhanitash et al. 2017). Yousuf et al. (2016) used a weak anion resin, Amberlite IRA-67 and granulated activated carbon Norit type Darco. In contrast to the other research, Yousuf et al. (2016) found that a pH below the pKa was beneficial for both investigated resins, with both resins offering significant acid recovery yields of 74% for Amberlite IRA-67 and 63% for the activated carbon, at 200 $g_{adsorbent}\ L_{broth}^{-1}$. This is due to the hydrophobic interactions dominating over the ion-exchange interactions.

Due to the wide range of resins with varying interaction types, it should be possible to find a resin to match the optimum fermentation conditions or vice versa. For example, with Amberlyst A21 and grape pomace AF pH 6.5 was best for recovery (Rebecchi et al. 2016).This is because the pH affects the concentration of active protonated amino groups on this resin, so as the pH increases the concentration of pronated amino groups decreases thereby decreasing the number of sites available for adsorption of the VFA (Rebecchi et al. 2016). Co-optimization of the fermentation and adsorption step would be beneficial.

The other key step associated with adsorption is desorption. This was not considered by Yousuf et al. (2016). Rebecchi et al. (2016) decided upon solvent based desorption from the Amberlyst A21 resin. Ethanol demonstrated VFAs desorption rates of approximately 67%, and desorption of longer chain VFAs to be higher. Whereas water, as the solvent, had higher selectivity for shorter chain VFAs. Rebecchi et al. (2016) advocate ethanol as the best solvent since it is easier to recover the VFA through distillation due to lower boiling point compared to water. This also regenerates the ethanol for reuse. VFA desorption was further improved through the addition of 1 M NaOH to the ethanol or water. This is not surprising, as NaOH is a strong base, therefore can outcompete the amine-acid bond. This is similar to the back-extraction of acids into NaOH with membrane extraction (Rebecchi et al. 2016). Despite the improvement with the use of NaOH, the end use of the VFA needs to be considered. The addition of NaOH results in the VFAs being present as sodium salts. To achieve a free acid product, then acidification using a mineral acid is required (López-Garzón and Straathof 2014). Reyhanitash et al. (2017) decided upon nitrogen stripping at elevated temperatures (180 °C) for desorption. This desorption process could produce VFA purities of up to 91 wt% from a 0.25 wt% synthetic wastewater solution.

For Cabrera-Rodríguez et al. (2015, 2017b, 2017a) the desorption step was the main focus of their research. They developed a novel CO_2-expanded alcohol desorption process to allow the direct conversion of VFAs to esters. This research is one of only a few examples where the end product use has been considered prior to VFA recovery development. The conversion to esters was quicker for the shorter chain VFAs, with Cabrera-Rodríguez et al (2017a) suggesting that there was a steric factor involved.

3.4.2 *Distillation*

Distillation is a widely used separation method; separating liquids based on differences in boiling point/volatility. Mumtaz et al. (2008) proposed a two-stage distillation process for the recovery of mixed VFAs from AF of POME. The first stage is to dewater the fermentation broth to achieve a VFA concentrate which is acidified using sulphuric acid then distilled further to recover the VFAs in the distillate. Prior to the initial distillation, filtration of the broth is required to allow biomass recycling as the high temperatures (>105 °C) will kill the microorganisms. The broth contained 10 g VFA L^{-1} was concentrated to 55 g VFA L^{-1} after the two-stage distillation process. This is still a relatively low concentration, as it is equivalent to the ones achieved in some fermentation processes. The biggest problem with implementing distillation is that water is the major fermentation broth component with a lower boiling point than the VFAs, Table 1. This makes distillation an energy intensive recovery process. Unless the concentration can be significantly improved, or heat integration is possible, this energy demand plus the addition of another concentration step will likely render distillation technology unfavorable for VFAs recovery.

3.4.3 *Electrocoagulation*

Fayad et al. (2017) proposed electrocoagulation as a primary separation method for the purification of VFAs from digestate or AF. Electrocoagulation works by supplying a current to sacrificial electrodes, e.g. aluminium or iron, which produce metal ions to induce flocculation of organic matter and nutrients. This is, therefore, predominantly a means of solid and contaminant removal and should be considered as an alternative to filtration or centrifugation. Fayad et al.

(2017) demonstrated VFAs are not flocculated in this process, remaining in solution at a constant concentration, requiring further recovery. From a glucose fermentation this technology could remove >80% of solids, nitrogenous and phosphorous species from the fermentation broth. They also demonstrate this method has the potential to be more cost effective than electrodialysis and nanofiltration (Fayad et al. 2017), but electrocoagulation does not concentrate the VFA solution.

3.4.4 Electrodialysis

Electrodialysis (ED) is the most researched separation technique for VFA recovery, with many different operating methods. It is often proposed as it requires the VFAs to be in their charged form, therefore can operate at typical fermentation pH (Table 3). A series of charged membranes are positioned between two electrodes, and a current is applied across them to facilitate ion transfer creating a VFA-rich (concentrate) chamber (Jones et al. 2015). Huang et al. (2007) provide a detailed overview of electrodialysis for the recovery of organic acids.

Conventional (CED) is the most researched ED method for VFA recovery (Jones et al. 2015, 2017; Scoma et al. 2016; Tao et al. 2016; Domingos et al. 2018; Pan et al. 2018). All of the research demonstrates that CED can remove VFAs from the fermentation broth, with 95% VFA recovery achieved by Jones et al. (2015) and 92% by Tao et al. (2016). CED also demonstrated a preference towards acetic acid recovery compared to other VFAs. The general order of selectivity was HAc > HPr > HBu > iHBu > HVa > HHex (Jones et al. 2015; Scoma et al. 2016; Pan et al. 2018). This would be advantageous if acetic acid or other smaller chain VFAs were the desired product. The benefit of this would be that the longer VFAs could be fed back to the reactor for degradation to acetic acid, then removed.

Various increases in the recovered VFA concentration, due to ED, are reported: Tao et al. (2016) stated that the VFA concentration increased from 11.73 g L^{-1} to 19.82 g L^{-1}, which was in agreement with Scoma et al. (2016) who reported a concentration increase by a factor of 1.2–1.5. Pan et al. (2018) reported a 3–4 fold increase in VFA concentration. This bigger increase is due to the lower initial concentration of VFA in the feed chamber, but the overall VFA concentration in the product/concentrate chamber only reached approximately 6 g L^{-1} in nearly 550 h of operation. In practice, these concentrations <2 wt% are too low to use the VFA as a feedstock for other fermentation processes, concentrations of 200–500 g L^{-1} would be desirable.

Electrodialysis with bipolar membranes (EDBM) systems have also been tested for VFA recovery. Zhang and Angelidaki (2015) have proposed a microbial bipolar electrodialysis cell (MBEDC); the anode utilizes a biofilm to convert organic compounds into H^+ ions and carbon dioxide, reducing the electricity use compared to alternative ED systems. Arslan et al. (2017) proposed a more traditional EDBM system; they suggest one of the advantages of using bipolar membranes is that the alkalinity/pH in the system can be controlled by supplying hydroxide ions to the fermentation. The VFA recovery performance of these systems was similar to CED, with Zhang and Angelidaki (2015) achieving 95% VFA recovery and Arslan et al. (2017) achieving 69%. The disadvantage of bipolar membrane systems is the cost associated with membrane maintenance and replacement (Arslan et al. 2017).

A major disadvantage with all ED processes is the preferential removal of non-VFA anions, such as Cl^-. They are smaller than the VFA anions, therefore faster transfer into the concentrate is observed (Zhang and Angelidaki 2015; Scoma et al. 2016; Tao et al. 2016; Arslan et al. 2017; Domingos et al. 2018). Additionally, many ED processes require additional salts, typically sodium chloride, to be added to improve the concentration gradients for mass transfer (Zhang and Angelidaki 2015). This practice will not only complicate further downstream processing, but it may make this stream unsuitable as a fermentation feedstock, depending on the secondary fermentation microorganisms' tolerance to these ions.

In the majority of research performed, highly clarified fermentation broths are used with the ED system. Generally, the broth is centrifuged/screened then filtered before ED (Jones et al. 2015; Tao et al. 2016; Domingos et al. 2018). This is because fouling of the membranes is reported to increase electrical resistance (Jones et al. 2015). Additionally, although it is suggested that the process is in a position to be integrated with fermentation for solids/effluent recycling (i.e. ISPR), none of the research has demonstrated this. Instead, a batch fermentation is performed

followed by batch clarification and batch ED (Tao et al. 2016; Domingos et al. 2018).

3.4.5 Esterification

Ester production is one of the major uses of VFAs. If the esterification occurs as part of the separation process, it could increase the product routes from waste substrates. Plácido and Zhang (2018a) investigated the conversion of VFAs from fermentation broth into methyl esters, and proposed that ammonium sulphate could be produced as a byproduct due to acidification of the broth using sulphuric acid, which could increase the plant profitability. The dilute VFA concentration in the fermentation broth (100 g_{VFA} L^{-1}) would, however, hinder the direct esterification process. For a VFA concentration of 500 g_{VFA} L^{-1}, the methyl VFA yield was less than 10%. Yields of 50% were possible with a VFA concentration of 80% (800 g_{VFA} L^{-1}). At these yields, an organic phase formed which would improve the separation and recovery of esters from the fermentation broth (Plácido and Zhang 2018a). This would require a considerable concentration step prior to esterification; therefore esterification is more suited as a secondary downstream step rather than a primary separation step.

3.4.6 Filtration

The integration of filtration with AF is one of the most researched separation methods. There are two motives for this: solid separation (prior to further VFA recovery) and selective separation of VFA based on molecular size.

For selective VFA separation, nanofiltration (NF) is proposed, although the conclusions of this research are mixed. Zacharof and Lovitt (2014) found that the VFAs remained in the retentate, with retention ratios up to 75%. This enabled the concentration of acetic acid and butyric acid to increase by a factor of 2.5 and 1.8 respectively. The pH was found to influence the flux, productivity and retention, with optimum conditions at pH 7. In reality, this is a concentration step, and a solid removal step is required prior to nanofiltration to achieve a concentrated VFA solution in the retentate. Other soluble compounds are likely to remain, and these impurities could limit the final VFA product options. In contrast, Xiong et al. (2015) optimized the nanofiltration step to reject sugars (>90%) with 0–40% rejection of VFAs, except for butyric acid where 100% was rejected. When they integrated this process with AD, the acid concentration in the reactor was reduced by nearly 90%, meaning that 86% of the acids produced were recovered. Operation of nanofiltration in this mode would be easier to integrate with the fermentation, as the retentate can be recycled back to the reactor for further COD reduction. Unfortunately, no information on the permeate concentrations was reported. It must be noted that, similar to Zacharof and Lovitt (2014), Xiong et al. (2015) centrifuged and filtered the fermentation broth prior to nanofiltration to remove solids and reduce fouling of the membrane. Therefore, this nanofiltration process should be considered as a VFA purification step rather than VFA recovery.

Jung et al. (2015) propose using forward osmosis (FO), whereby a concentration gradient is established using a concentrated salt draw solution. This process cannot be considered a true VFA recovery process (for ISPR) as the VFAs remain in the retentate and the water is transferred to the draw solution, similar to the nanofiltration by Zacharof and Lovitt (2014). With this FO process, there was a 97% VFA rejection and the concentration was increased to 49.28 g_{VFA} L^{-1} from 35.12 g_{VFA} L^{-1} in the fermentation broth (a factor of 1.4), at an optimum pH of 8. A techno-economic comparison between nanofiltration and FO operation is required, to see if there are any justifiable benefits, as the added requirement of a draw solution and regeneration of the draw solution will increase operating costs.

3.4.7 Freeze/thaw separation

Freezing followed by thawing is a physical separation method proposed by Omar et al. (2009) as an initial step in the recovery of organic acids from AF. They froze the fermentation broth overnight at −30 °C, followed by thawing at 60 °C for 2–3 h on a cloth mesh with a 1 mm pore size. They removed 66% of the suspended solids and saw the acid concentration increase from 59 g L^{-1} to 70 g L^{-1}, an increase of 16%. Further processing steps were then applied (centrifugation, filtration and evaporation) to further concentrate the acids. The freeze–thaw process, however, is effectively a solid removal step, as other solubles such as nitrogen-based compounds were not removed from the broth (Omar et al. 2009).

3.4.8 Gas stripping

Gas stripping involves sparging a gas through the fermentation broth to transfer volatile products from the liquid phase to the gas phase, from which they can be recovered. For gas stripping to be effective, the VFAs must be present in their undissociated form. Li et al. (2015) achieved this by operating the fermentation below pH 4.8 (average VFA pKa). They conditioned their inoculum to operate under acidic pH, by dosing the anaerobic sludge with glucose to facilitate rapid VFA accumulation. The gas stripping was cyclic, only occurring when the pH was reduced below 4.8; ensuring that more than 50% of the VFAs were present in the undissociated form. The headspace gas, predominantly nitrogen, was circulated through the fermentation broth and a calcium carbonate slurry to capture the VFAs. The pH of the fermentation broth increased, indicating removal of VFA from the fermentation broth. The analysis of the liquid portion of the calcium carbonate slurry confirmed that VFA salts were present, with butyric acid being the most abundant (Li et al. 2015). This initial assessment of gas stripping for VFA recovery has positive results, but similarly to the majority of recovery techniques, it relies on the pH being less than the pKa (Table 4). Whilst Li et al. (2015) achieved this through conditioning the fermentation to operate below pH 4.8 this is not a typical operating pH for AF, Table 3. In addition, the authors did not propose an end use for the VFA-calcium salts.

3.4.9 Liquid–liquid extraction

Liquid–liquid extraction (LLE) is a well-understood industrial technique, where two immiscible phases are in contact and the product is selectively transferred from one phase to the other driven by chemical potential. Kertes et al. (2009) provide a detailed overview of the mechanisms behind LLE for carboxylic acids.

LLE was the first proposed technique for mixed VFA recovery by Mostafa (1999). This work focused on developing a method to combine LLE with AF. Tri-n-octylphosphine (TOPO) dissolved in kerosene was used as an extractant and diluent respectively. They demonstrated that it was possible to recover over 75% of VFA in the fermentation broth in under 2 h, when extractant: diluent ratio, extractant: fermentation broth ratio, extraction temperature and mixing rate were optimized. Alkaya et al. (2009) also used TOPO in kerosene, but focused on the influence of pH on recovery. At pH 2.5, the total VFA recovery efficiency was 67% with 20% TOPO in kerosene, at pH 5.5 this decreased to 32% due to less VFA being available in the free acid form. Reyhanitash et al. (2016) investigated the use of trioctylamine (TOA) in n-octanol, and several phosphonium ionic liquids as possible extractants. pH was, again, a controlling factor in VFA recovery for both these extractants. It is well established that for affinity based separation techniques such as LLE the acid is required to be in its protonated form, therefore requiring the pH to be lower than the pKa of the acid. This is a significant problem for AF, where the fermentation pH tends to be higher than the pKa.

Non-reactive extractants have also been investigated. Bekatorou et al. (2016) considered a selection of organic solvents, in particular alcohols. This would allow for direct esterification of the VFAs without the need for a second step to remove the acid from the extractant. This is an interesting approach; generally, the extractant choice is an organic solvent similar to the solute e.g. alcohols to recover alcohols from the aqueous phase (Rocha et al. 2017). As expected, the pH of the VFA solution had a significant effect on the recovery efficiency. Bekatorou et al. (2016) suggested the use of 2-pentanol, which had the best performance achieving 85% VFA recovery; or 1-butanol, which, although had a lower recovery percentage (65–78%), can be biologically produced enabling truly biobased esters.

Rocha et al. (2017) suggested using MCFAs such as hexanoic, octanoic and decanoic acid as non-reactive extractants. As MCFAs are partially soluble in water, an inexpensive diluent such as toluene or n-hexane is required to facilitate extraction. The MCFAs present both hydrogen bond donors and acceptors; therefore, have the potential to address the acid functionality of the VFAs. One of the key factors in this research was diluent selection, as n-hexane decreased the number of dimerization sites between the MCFA and VFA, therefore reduced the extraction potential. The other key outcome was that the addition of an MCFA extractant did not have a linear effect on the % recovery of VFA; pure hexane recovered 6% of the butyric acid, but 5% hexanoic acid in hexane resulted in 51% recovery. Further increases to 55% and 100%

hexanoic acid resulted in 80% and 85% recovery, respectively. This non-linear relationship could be beneficial to developing a recovery process with as low as possible economic footprint (Rocha et al. 2017). This is similar to the results observed by Alkaya et al. (2009) using TOPO in kerosene.

Ionic liquids (ILs) have been considered as an alternative to organic extractants. They have been shown to have higher distribution coefficients (the ratio of acid between the extractant phase and aqueous phase at equilibrium) for carboxylic acids at low concentrations, therefore ideal for the concentration ranges obtained via AF. Additionally their high boiling and decomposition temperatures allow for regeneration by evaporative methods (Reyhanitash et al. 2018). Reyhanitash et al. (2016) demonstrated that ILs, in particular trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate ($[P_{666,14}][Phos]$) could produce a more concentrated VFA stream, 62.9 wt% total VFA, compared to 50.2 wt% total VFA with 20 wt% TOA in n-octanol, which would allow for lower solvent to feed ratios. Similar to organic extractants, the mechanism of recovery is primarily hydrogen bonding, requiring the VFA to be in their free acid form (Reyhanitash et al. 2016). The use of ILs as an extractant for VFA recovery has only been tested with synthetic VFA mixtures, rather than real AF broth. Reyhanitash et al. (2016) considered the impact of different salts present in waste water on the extraction process, which influence the choice of IL. The addition of salts caused a reduction in the distribution coefficient of acetic acid between the broth and extractant, with all extractants. It is believed that the salt anions form complexes with the extractant reducing the availability for extraction of the acid. This observation was also made with 20 wt% TOA in n-octanol. Reyhanitash et al. (2016) observed that careful selection of the IL anion was required. Cl^- and Br^- anions were found to leach significantly into the fermentation broth, resulting in an ion exchange mechanism for extraction of the VFA. This results in an irreversible extraction, as the VFA cannot be recovered without replacing the leached Cl^- or Br^- ions. Anions such as phosphate did not significantly leach into the fermentation broth, therefore are a better extractant. IL regeneration methods have been studied by Reyhanitash et al. (2019), based on an acetic acid concentrations of 1 wt% in the broth, the back extraction with a volatile base such as ammonia or trimethylamine allowing for recovery of the free acid reducing further downstream processing. They were able to produce a final product stream with 90 wt% acetic acid (10 wt% water). The impact of real fermentation broth on the IL and the subsequent regeneration needs to be considered.

Overall, LLE appears to be a promising recovery technique. All LLE research indicates: that pH < pKa is beneficial; selectivity is higher for longer chain acids, although recovery of acetic acid is possible; and a larger ratio of extractant to diluent is more effective, but less economically favorable. Most of the research using real fermentation broth required a clarification step (filtration or centrifugation) prior to extraction, research into the necessity of this step is advised to understand the scale up requirements. Additionally, existing research does not, typically, comment on the concentration of VFA in the extractant or how to recover the VFA from it. Reyhanitash et al. (2018) have performed an initial review and process assessment of extractant regeneration, indicating that all methods require more energy for separation than the heat of combustion for VFAs potentially limiting the industrial applicability based on the current developmental states.

3.4.10 Membrane extraction

Membrane extraction is an extension of LLE, whereby a membrane is placed between the aqueous feed and extractant. Typically, to recover carboxylic acids, membrane extraction utilizes a hydrophobic porous membrane with an organic extractant such as TOPO or TOA in a diluent (Solichien et al. 1995; Vajda et al. 2003). Once the extractant is acid-rich, it is passed across a second membrane extraction unit, where a concentrated sodium hydroxide stripping solution is used to regenerate the extractant and return the carboxylic acid to the aqueous phase (Schlosser et al. 2005). To achieve the carboxylic acid as a free acid in the aqueous phase, the VFA-sodium hydroxide solution would need to be re-acidified with a mineral acid, such as sulphuric acid. This will produce a mineral salt that will need to be disposed of or found a use for (López-Garzón and Straathof 2014).

For recovery of VFA, Plácido and Zhang (2018a) followed the traditional method of membrane assisted extraction using a polypropylene porous membrane with TOA in 1-octanol. They achieved 80% recovery

of all acids other than acetic acid, from acidified fermentation broth, in 24 h of operation. This could lead to selective recovery of VFA, which could be beneficial, depending on the final product use. The downside to this work is that the fermentation broth needed to be acidified prior to membrane extraction; this is the same as other affinity separation techniques.

Alternatively the organic extraction step can be eliminated, and a sodium hydroxide solution is used as the extractant. A hydrophobic polytetrafluoroethylene (PTFE) membrane separates the two aqueous phases, with the pores remaining air-filled to ensure separation of only the volatile products. Acidification of the fermentation broth from pH 6.6 to 3 saw a 65 times increase in the overall mass transfer coefficient achieved for butyric acid (Yesil et al. 2014; Tugtas 2014). Aydin et al. (2018) found that there was no selective recovery with air-filled pores and established that filling the pores with an organic extractant increases the selectivity for VFA. There are still questions, however, as to the long-term stability and operation of utilizing an extractant-filled membrane.

These membrane extraction methods result in multiple downstream processing steps, with high mineral acid and base consumption rates to transfer the VFAs to the final aqueous phase. To reduce the downstream processing steps Outram and Zhang (2018) demonstrated that a non-porous silicone membrane with a water extractant can selectively recover larger chain VFAs, from an acidified fermentation broth. Using water as the extractant, means that the VFAs are present in an aqueous solution, therefore reducing the number of downstream processing steps. The direct use of a real fermentation broth, without any large (>1 mm) solids removal step, did not impede product recovery as improved mass transfer coefficients were observed compared to a synthetic VFA solution. The use of a non-porous membrane hindered the mass transfer compared to porous membrane alternatives with a sodium hydroxide extractant. Therefore, a larger membrane area is required for the same VFA flux, but this is offset against the negligible extractant cost and decreased downstream processing. Dessì et al (2020) applied this method to a cheese whey dark fermentation, and was able to recover butyric acid achieving concentrations of 2.5 g L^{-1} and greater than 90% purity of the recovered products (pH 5). The high purity reduced as fermentation broth pH decreased to 3, but sugars, nutrients, and lactic acid did not cross the membrane therefore facilitating an easier downstream recovery.

3.4.11 Pervaporation

Pervaporation separates volatile components across a membrane which is subjected to a vacuum, or sweep gas, on the permeate side. The membrane material selectively separates the products based on diffusion.

Choudhari et al. (2015) developed a novel polyether block amide (PEBA) graphene composite membrane for pervaporation, with focusing on butyric acid recovery. The pervaporation unit was tested on digestate taken from AD of perennial grass and dairy wastewater. Like many other techniques, the broth was microfiltered followed by an ultrafiltration step (10,000 MWCO), then acidified to pH 3.7. Even with this degree of solids removal, a decrease in flux was observed compared to pervaporation of a synthetic broth. Results showed that the butyric acid concentration could be increased from 6 g L^{-1} to 114 g L^{-1} (19 times increase). When considering the separation factor (ratio of VFA and water in the permeate divided by the ratio of VFA and water in the feed), valeric acid was higher than butyric acid indicating that pervaporation with PEBA composite membranes has higher selectivity for larger, more hydrophobic VFAs.

Yesil et al. (2018) considered three membranes for the recovery of VFAs using synthetic broth: polytetrafluoroethylene (PTFE), PTFE filled with tridodecylamine (TDDA) and a silicone-PTFE composite. They found the TDDA filled PTFE membrane to offer the highest VFA flux and separation factor. This is due to the VFAs forming a complex with the TDDA in the membrane. The separation mechanism resembles extraction more than evaporation and diffusion.

VFAs have a greater affinity to water than other fermentation products such as alcohols; this will make any separation based on volatility harder. All the membranes used, except PTFE, are in the research phase of development which makes it difficult to compare with commercial pervaporation processes. Additionally, Choudhari et al. (2015) and Yesil et al. (2018) did not consider the ease of product capture (in a commercially viable method) from the vapor phase. This step could lead to significant product loss if not carefully considered or investigated.

3.4.12 Salting-out and salting-out extraction

The addition of a salt to facilitate phase separation is common practice. Fu et al. (2015, 2017) have investigated this as a method to help improve the extraction of VFAs from synthetic broth. The selection of the optimum salt-extractant combination plays a major role. Fu et al. (2015) initially investigated the separation of carboxylic acids, from a mixture containing formic, acetic, propionic, lactic, succinic and citric acids, using an ethanol-ammonium sulphate combination. This system was more effective for the extraction of the VFAs compared to acids with multiple OH groups (e.g. lactic or succinic acid), as the latter are more hydrophilic. Like LLE, decreasing the pH resulted in an increase in the partition of acid in the organic phase.

The salting-out extraction for a butyric and acetic acid mixture was also tested using monohydric alcohols with monosodium phosphate (Fu et al. 2017). It was initially shown that salting-out can induce phase separation, but the low acid concentration required high salt concentrations and the phase separation was difficult to observe. Therefore, an extractant was used to improve the separation. Earlier work had established that the free acid was required in LLE (hence pH $<$ pKa). With monosodium phosphate more phosphate ions were present as the pH increased to 6. The higher concentration of phosphate ions increased the salting-out capability of the system, hence an increase in acid separation was observed. This could potentially allow VFAs recovery without the need for acidification.

These examples of salting-out extraction, have used alcohols as the extractant. The salt addition improves the capability of the extractant, and reduces the degree of miscibility of the small alcohols (e.g. ethanol) in water. Both Fu et al. (2017) and Yan et al. (2018) considered a selection of low molecular weight alcohols. They demonstrated that as the hydrophobicity of the alcohol increased, the distribution of extracted acid decreased. Fu et al. (2017) achieved their highest distribution coefficient, 106, with an ethanol-monosodium phosphate system. For a 50 g L^{-1} butyric acid solution, with the addition of 23 wt% monosodium phosphate, 94% of the butyric acid was recovered.

The application of salting-out extraction for VFAs recovery is still in its very early stages. The next step is to apply it to VFA-rich fermentation broth. A salt concentration of 23 wt% is likely to be toxic to the bacteria used in AF, limiting direct integration with the fermentation broth for ISPR. External application could be a solution, but a salt recovery process will be required to minimize the amount of salt which is returned to the fermenter for further processing and reduce the cost of this unit operation.

3.4.13 Recovery technique comparison

As the recovery techniques have been developed independently of the fermentation, many of them require different conditions, Table 4, compared to the fermentation, Table 3. The two major factors slowing down the implementation of VFA ISPR are the degree of clarification and acidification required prior to recovery. Ideally, the primary recovery step should be applied directly to the fermentation broth. Many authors centrifuged and microfiltered the broth prior to the VFA recovery technique; this level of processing is likely to be unsustainable for scale up. Additionally, many authors adjust the pH prior to recovery through acidification to successfully recover VFAs, Table 4, but no consideration is made to the impact of this acidification step either technically or economically. For a continuous fermentation process it is advantageous to remove the VFAs and recycle the fermentation broth and solids back to the reactor for further processing to maximize yield, productivity, and waste destruction. For this, the broth needs to be neutralized, which will result in mineral salt formation. The impact of the acidification, neutralization and salt formation on the fermentation process needs to be investigated.

Membrane extraction, electrodialysis and filtration have been the most researched recovery techniques. It is not possible to select a single technique that should be the focus for future VFA recovery research. Selection of a recovery technique should consider: the fermentation conditions, major acid produced, ideal recovered form and end-product use. If the major fermentation acid is acetic acid then techniques which utilize the dissociated acid will have increased selectivity, such as electrodialysis. For longer chain VFAs, such as butyric acid, techniques that rely on the acid being in the undissociated form tend to be more favorable. Contemplating factors such as these in the

initial process design will enable faster, more targeted development of AF process.

3.5 Process economics

To date, there has been a very limited analysis of the economics driving the move from biogas to VFA production using waste substrates. There is a more diverse product range for VFAs than biogas, opening new markets as the search for alternatives to petrochemical-based products continues. The biggest difficulty with performing an economic analysis is the lack of defined process route. Bonk et al. (2015) overcame this by assuming a VFA sales price thereby stating the maximum permissible purification cost, which other researchers could use to justify their purification process. They assumed that the VFAs would be separated into their individual acids, creating numerous product streams. Using MSW as a feedstock resulted in a maximum purification cost of 14.96 USD $m^{-3}_{effluent}$ with no pretreatment and 15.5 USD $m^{-3}_{effluent}$ if pretreatment was used, due to increased VFA production. This was considered acceptable as purification cost of seawater via reverse osmosis is 1 USD $m^{-3}_{effluent}$, which involves the separation of water from a similar concentration of solute to VFA. Even though AF fermentation broth is more complex, the allowance for a purification cost ten times greater than seawater desalination should be satisfactory to overcome the challenges with VFA recovery. No analysis of VFA recovery and separation into individual acids could be found in the literature. The current research indicates that the production of VFAs has the potential to produce higher revenues than biogas production. Bastidas-Oyanedel and Schmidt (2018) confirm this with an economic analysis of a food waste biorefinery for the production of VFAs (in particular acetic and butyric acid) compared to the more traditional AD with biogas upgrading. They found that the production of VFAs was more profitable, with a profit of 296 USD t_{VS}^{-1}, compared to 19 USD t_{VS}^{-1} for gas to grid AD. The downside to AF compared to AD was the increased operating costs for AF due to the complexity of separating the acids. This analysis provides a good starting point, encouraging researchers to diversify away from AD to VFA production. The economics will vary considerably depending on the specific process route and the eventual product market.

Many researchers assume that separation of the individual acids will not be required. Fasahati and Liu (2014) calculated that the minimum selling price of the mixed VFAs from brown algae would be 384 USD t^{-1}, which is lower than the market price for (petrochemical) acetic acid. Their process did not account for acidification of the fermentation broth which would be required for their selected recovery method, membrane distillation, or the final potential market of the mixed VFA solution. Liu et al (2018a) considered the production of VFAs from wastewater, to be used as the carbon source for the wastewater treatment plant's biological nutrient removal (BNR) process. They indicate that VFA production would increase profits 2.5 times that of biogas production. The increased profitability is related to smaller capital investment costs due to the shorter residence time of AF compared to AD, higher sales value, and direct use of VFAs, therefore, no expensive downstream processing is required. Fernández-Dacosta et al. (2015) considered the economics of VFAs for PHA production. They found that, compared to equivalent petrochemical plastics such as polyethylene terephthalate, PHA is not yet economically competitive. This is surprising as it is often the preferred route for mixed VFA use; but it highlights the importance of considering the economics of a process early on in the development. The process they investigated was relatively simple and they did not require a VFA recovery stage, which would normally have a high contribution to the operating costs.

The economic analysis has highlighted the importance of understanding the marketable product generated. The use of VFAs as a feedstock for other bioprocesses does not look favorable under current research developments. This should be reassessed with continuing developments in this field, and greater integration of the two bioprocesses is required. In the context of wastewater treatment plants, using VFAs as a feedstock for BNR appears to be the most promising application in the current development landscape, due to the direct integration of the two processes with minimal intermediate treatment. If this level of integration could be considered for other bioprocesses, then it might be possible to develop waste treatment plants into biorefineries and further integration into the circular economy. This is of interest to industry as demonstrated by large EU Horizon 2020 grants, VOLATILE (European Commision 2017a) and

URBIOFIN (European Commision 2017b), representing 35 different organizations and 12 EU countries. The early signs are that VFAs from waste have the potential to compete with petrochemical VFA, but more research is required for product use, fermentation optimization and development and integration of the downstream setup.

4 Progressing AF and VFA production

Current research is focused on either fermentation development or primary product recovery, with very little interaction between the two. For AF to offer competitive bio-VFAs to the market, research needs to be tailored with more thought to the end product and integrated process design. Current research is non-specific, rather than focus on maximizing general VFA yield or concentration, researchers should have specific/strategic aims for why they want to produce VFA—e.g. as a means of waste destruction or for the production of bio-VFAs as an alternative to petrochemicals. Researchers need to consider the use of the VFA—e.g. feedstock for fermentation or as individual acids as a bulk chemical (for use in other processes). This will enable more targeted fermentation optimization and process design. Additionally, this will allow for detailed techno-economic analyses to be performed.

Fermentation research needs to consider more advanced experimental designs. Naturally, AF will have high degrees of variability, from feedstocks (location and seasonal) through to inoculum source and microbiome present in the reactor. Technologies such as –omics analysis could help provide insight into making more generalized claims of how to optimize a fermentation towards the specific goal. The design process needs to account for the inherent variability which will be encountered—e.g. understanding the ideal operation space for pH and high nitrogen feedstocks (which cause an increase in pH) to maximize VFA yield and concentration. From recovery literature it is clear that a compromise will be required on optimum fermentation and product recovery conditions. Research needs to account for this within experimental design, therefore more integration of the two steps is required at laboratory scale. The final product use should also be considered when designing the recovery method. The conditions required for any proceeding downstream unit operations could influence the selection of the primary recovery step.

5 Conclusion

It is well-established that biobased production of building block chemicals is beneficial for achieving a circular economy. The production of VFAs from waste sources or biomass from non-human consumption energy crops can help achieve this. Existing research has demonstrated the potential of acidogenic fermentation, and progress is being made for both upstream and downstream processing. Future research needs to look at whole process design, from feedstock pretreatment through fermentation and product recovery to routes into the market. This requires establishing more strategic, multidisciplinary research projects to further progress AF and bio-VFA production, and utilizing more sophisticated research and operation tools to enable a better understanding of the process and adaption to the inherent variability in the process.

Acknowledgements The authors would like to thank Prof. Sonia Heaven for her insightful advice, guidance, and feedback during the preparation of this manuscript.

Author contributions Maria Ramos Suarez: Conceptualization, Methodology, Writing—Original Draft, Writing—Review and Editing. Yue Zhang: Conceptualization, Writing—Review and Editing, Supervision, Funding acquisition. Victoria Outram: Conceptualization, Methodology, Writing—Original Draft, Writing—Review and Editing, Supervision.

Funding This work was funded by the Engineering and Physical Sciences Research Council (1950351: 'Integrated biorefinery products from wastes and residues') and Fiberight Ltd (MRS); and the Newton Fund Institutional Links Grant (275880329: 'Development of a bio-refinery system for organic acid production, bioenergy generation and nutrient recovery using fish wastes from Tumaco, Colombia') delivered by the British Council (VO).

Availability of data and material Data supporting this study are openly available at doi.org/10.6084/m9.figshare.11854857.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Ai B, Li J, Song J et al (2013) Butyric acid fermentation from rice straw with undefined mixed culture: Enrichment and selection of cellulolytic butyrate-producing microbial community. Int J Agric Biol 15:1075–1082

Alibaba (2018) Chinese E-Commerce. https://www.alibaba.com/. Accessed 25 April 2018

Alkaya E, Demirer GN (2011) Anaerobic acidification of sugar-beet processing wastes: effect of operational parameters. Biomass Bioenergy 35:32–39. https://doi.org/10.1016/j.biombioe.2010.08.002

Alkaya E, Kaptan S, Ozkan L et al (2009) Recovery of acids from anaerobic acidification broth by liquid–liquid extraction. Chemosphere 77:1137–1142. https://doi.org/10.1016/j.chemosphere.2009.08.027

Allison BJ, Cádiz JC, Karuna N et al (2016) The effect of ionic liquid pretreatment on the bioconversion of tomato processing waste to fermentable sugars and biogas. Appl Biochem Biotechnol 179:1227–1247. https://doi.org/10.1007/s12010-016-2061-4

Alzate ME, Muñoz R, Rogalla F et al (2012) Biochemical methane potential of microalgae: influence of substrate to inoculum ratio, biomass concentration and pretreatment. Bioresour Technol 123:488–494. https://doi.org/10.1016/j.biortech.2012.06.113

Ariunbaatar J, Panico A, Esposito G et al (2014) Pretreatment methods to enhance anaerobic digestion of organic solid waste. Appl Energy 123:143–156. https://doi.org/10.1016/j.apenergy.2014.02.035

Ariunbaatar J, Panico A, Yeh DH et al (2015) Enhanced mesophilic anaerobic digestion of food waste by thermal pretreatment: substrate versus digestate heating. Waste Manag 46:176–181. https://doi.org/10.1016/j.wasman.2015.07.045

Arslan D, Steinbusch KJJ, Diels L et al (2013) Selective carboxylate production by controlling hydrogen, carbon dioxide and substrate concentrations in mixed culture fermentation. Bioresour Technol 136:452–460. https://doi.org/10.1016/j.biortech.2013.03.063

Arslan D, Steinbusch KJJ, Diels L et al (2016) Selective short-chain carboxylates production: a review of control mechanisms to direct mixed culture fermentations. Crit Rev Environ Sci Technol 46:592–634. https://doi.org/10.1080/10643389.2016.1145959

Arslan D, Zhang Y, Steinbusch KJJ et al (2017) In-situ carboxylate recovery and simultaneous pH control with tailor-configured bipolar membrane electrodialysis during continuous mixed culture fermentation. Sep Purif Technol 175:27–35. https://doi.org/10.1016/j.seppur.2016.11.032

Atasoy M, Cetecioglu Z (2020) Butyric acid dominant volatile fatty acids production: bio-augmentation of mixed culture fermentation by *Clostridium butyricum*. J Environ Chem Eng 8:104496. https://doi.org/10.1016/j.jece.2020.104496

Atasoy M, Eyice O, Schnürer A, Cetecioglu Z (2019) Volatile fatty acids production via mixed culture fermentation: revealing the link between pH, inoculum type and bacterial composition. Bioresour Technol 292:121889. https://doi.org/10.1016/j.biortech.2019.121889

Atasoy M, Eyice O, Cetecioglu Z (2020) A comprehensive study of volatile fatty acids production from batch reactor to anaerobic sequencing batch reactor by using cheese processing wastewater. Bioresour Technol 311:123529. https://doi.org/10.1016/j.biortech.2020.123529

Aydin S, Yesil H, Tugtas AE (2018) Recovery of mixed volatile fatty acids from anaerobically fermented organic wastes by vapor permeation membrane contactors. Bioresour Technol 250:548–555. https://doi.org/10.1016/j.biortech.2017.11.061

Bastidas-Oyanedel J-R, Schmidt J (2018) Increasing profits in food waste biorefinery: a techno-economic analysis. Energies 11:1551. https://doi.org/10.3390/en11061551

Baumann I, Westermann P (2016) Microbial production of short chain fatty acids from lignocellulosic biomass: current processes and market. Biomed Res Int 2016:1–15. https://doi.org/10.1155/2016/8469357

Beccari M, Bertin L, Dionisi D et al (2009) Exploiting olive oil mill effluents as a renewable resource for production of biodegradable polymers through a combined anaerobic-aerobic process. J Chem Technol Biotechnol 84:901–908. https://doi.org/10.1002/jctb.2173

Bekatorou A, Dima A, Tsafrakidou P et al (2016) Downstream extraction process development for recovery of organic acids from a fermentation broth. Bioresour Technol 220:34–37. https://doi.org/10.1016/j.biortech.2016.08.039

Ben M, Mato T, Lopez A et al (2011) Bioplastic production using wood mill effluents as feedstock. Water Sci Technol 63:1196. https://doi.org/10.2166/wst.2011.358

Bengtsson S, Hallquist J, Werker A, Welander T (2008a) Acidogenic fermentation of industrial wastewaters: effects of chemostat retention time and pH on volatile fatty acids production. Biochem Eng J 40:492–499. https://doi.org/10.1016/j.bej.2008.02.004

Bengtsson S, Werker A, Christensson M, Welander T (2008b) Production of polyhydroxyalkanoates by activated sludge treating a paper mill wastewater. Bioresour Technol 99:509–516. https://doi.org/10.1016/j.biortech.2007.01.020

Bharathiraja B, Sudharsana T, Jayamuthunagai J et al (2018) Biogas production: a review on composition, fuel properties, feed stock and principles of anaerobic digestion. Renew Sustain Energy Rev 90:570–582. https://doi.org/10.1016/j.rser.2018.03.093

Bhatia SK, Yang Y-H (2017) Microbial production of volatile fatty acids: current status and future perspectives. Rev Environ Sci Bio/Technol 16:327–345. https://doi.org/10.1007/s11157-017-9431-4

Blasig JD, Holtzapple MT, Dale BE et al (1992) Volatile fatty acid fermentation of AFEX-treated bagasse and newspaper by rumen microorganisms. Resour Conserv Recycl 7:95–114. https://doi.org/10.1016/0921-3449(92)90009-Q

Bolzonella D, Fatone F, Pavan P, Cecchi F (2005) Anaerobic fermentation of organic municipal solid wastes for the production of soluble organic compounds. Ind Eng Chem Res 44:3412–3418. https://doi.org/10.1021/ie048937m

Bonk F, Bastidas-Oyanedel J-R, Schmidt JE (2015) Converting the organic fraction of solid waste from the city of Abu Dhabi to valuable products via dark fermentation: Economic and energy assessment. Waste Manag 40:82–91. https://doi.org/10.1016/j.wasman.2015.03.008

Borja R, Banks CJ, Sánchez E (1996) Anaerobic treatment of palm oil mill effluent in a two-stage up-flow anaerobic sludge blanket (UASB) system. J Biotechnol 45:125–135. https://doi.org/10.1016/0168-1656(95)00154-9

Brodeur G, Yau E, Badal K et al (2011) Chemical and physicochemical pretreatment of lignocellulosic biomass: a review. Enzyme Res 2011:1–17. https://doi.org/10.4061/2011/787532

Cabrera-Rodríguez CI, van der Wielen LAM, Straathof AJJ (2015) Separation and catalysis of carboxylates: byproduct reduction during the alkylation with dimethyl carbonate. Ind Eng Chem Res 54:10964–10973. https://doi.org/10.1021/acs.iecr.5b02911

Cabrera-Rodríguez CI, Moreno-González M, de Weerd FA et al (2017a) Esters production via carboxylates from anaerobic paper mill wastewater treatment. Bioresour Technol 237:186–192. https://doi.org/10.1016/j.biortech.2017.02.030

Cabrera-Rodríguez CI, Paltrinieri L, de Smet LCPM et al (2017b) Recovery and esterification of aqueous carboxylates by using CO_2: expanded alcohols with anion exchange. Green Chem 19:729–738. https://doi.org/10.1039/C6GC01391K

Cesaro A, Belgiorno V (2014) Pretreatment methods to improve anaerobic biodegradability of organic municipal solid waste fractions. Chem Eng J 240:24–37. https://doi.org/10.1016/j.cej.2013.11.055

Chen Y, Jiang X, Xiao K et al (2017) Enhanced volatile fatty acids (VFAs) production in a thermophilic fermenter with stepwise pH increase: investigation on dissolved organic matter transformation and microbial community shift. Water Res 112:261–268. https://doi.org/10.1016/j.watres.2017.01.067

Choudhari SK, Cerrone F, Woods T et al (2015) Pervaporation separation of butyric acid from aqueous and anaerobic digestion (AD) solutions using PEBA based composite membranes. J Ind Eng Chem 23:163–170. https://doi.org/10.1016/j.jiec.2014.08.010

Chynoweth DP, Turick CE, Owens JM et al (1993) Biochemical methane potential of biomass and waste feedstocks. Biomass Bioenergy 5:95–111. https://doi.org/10.1016/0961-9534(93)90010-2

Colombo B, Favini F, Scaglia B et al (2017) Enhanced polyhydroxyalkanoate (PHA) production from the organic fraction of municipal solid waste by using mixed microbial culture. Biotechnol Biofuels. https://doi.org/10.1186/s13068-017-0888-8

European Commision (2017a) Biowaste derived volatile fatty acid platform for biopolymers, bioactive compounds and chemical building blocks (VOLATILE). https://cordis.europa.eu/project/rcn/206563_en.html. Accessed 7 Oct 2018

European Commision (2017b) Demonstration of an integrated innovative biorefinery for the transformation of Municipal Solid Waste (MSW) into new BioBased products (URBIOFIN). https://cordis.europa.eu/project/rcn/210297_en.html. Accessed 10 Jul 2018

Dahiya S, Sarkar O, Swamy YV, Venkata Mohan S (2015) Acidogenic fermentation of food waste for volatile fatty acid production with co-generation of biohydrogen. Bioresour Technol 182:103–113. https://doi.org/10.1016/j.biortech.2015.01.007

De Groof V, Coma M, Arnot T et al (2019) Medium chain carboxylic acids from complex organic feedstocks by mixed culture fermentation. Molecules 24:398. https://doi.org/10.3390/molecules24030398

Deepanraj B, Sivasubramanian V, Jayaraj S (2017) Effect of substrate pretreatment on biogas production through anaerobic digestion of food waste. Int J Hydrogen Energy 42:26522–26528. https://doi.org/10.1016/j.ijhydene.2017.06.178

Dessì P, Asunis F, Ravishankar H et al (2020) Fermentative hydrogen production from cheese whey with in-line, concentration gradient-driven butyric acid extraction. Int J Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2020.06.081

Dhar BR, Nakhla G, Ray MB (2012) Techno-economic evaluation of ultrasound and thermal pretreatments for enhanced anaerobic digestion of municipal waste activated sludge. Waste Manag 32:542–549. https://doi.org/10.1016/j.wasman.2011.10.007

Dionisi D, Silva IMO (2016) Production of ethanol, organic acids and hydrogen: an opportunity for mixed culture biotechnology? Rev Environ Sci Bio/Technol 15:213–242. https://doi.org/10.1007/s11157-016-9393-y

Dionisi D, Carucci G, Papini MP et al (2005) Olive oil mill effluents as a feedstock for production of biodegradable polymers. Water Res 39:2076–2084. https://doi.org/10.1016/j.watres.2005.03.011

Dolan T, Cook MB, Angus AJ (2011) Financial appraisal of wet mesophilic AD technology as a renewable energy and waste management technology. Sci Total Environ 409:2460–2466. https://doi.org/10.1016/j.scitotenv.2011.03.011

Domingos JMB, Puccio S, Martinez GA et al (2018) Cheese whey integrated valorisation: production, concentration and exploitation of carboxylic acids for the production of polyhydroxyalkanoates by a fed-batch culture. Chem Eng J 336:47–53. https://doi.org/10.1016/j.cej.2017.11.024

Dong B, Gao P, Zhang D et al (2016) A new process to improve short-chain fatty acids and bio-methane generation from waste activated sludge. J Environ Sci 43:159–168. https://doi.org/10.1016/j.jes.2015.10.004

Elbeshbishy E, Hafez H, Dhar BR, Nakhla G (2011) Single and combined effect of various pretreatment methods for

biohydrogen production from food waste. Int J Hydrogen Energy 36:11379–11387. https://doi.org/10.1016/j.ijhydene.2011.02.067

Elgharbawy AA, Alam MZ, Moniruzzaman M, Goto M (2016) Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass. Biochem Eng J 109:252–267

Fasahati P, Liu J (2014) Techno-economic analysis of production and recovery of volatile fatty acids from brown algae using membrane distillation. In: Eden MR, Siirola JD, Towler GP (eds) Computer aided chemical engineering. Elsevier, Amsterdam, pp 303–308

Fayad N, Yehya T, Audonnet F, Vial C (2017) Preliminary purification of volatile fatty acids in a digestate from acidogenic fermentation by electrocoagulation. Sep Purif Technol 184:220–230. https://doi.org/10.1016/j.seppur.2017.04.041

Fdez-Güelfo LA, Álvarez-Gallego C, Sales D, Romero LI (2011) The use of thermochemical and biological pretreatments to enhance organic matter hydrolysis and solubilization from organic fraction of municipal solid waste (OFMSW). Chem Eng J 168:249–254. https://doi.org/10.1016/j.cej.2010.12.074

Feng L, Yan Y, Chen Y (2011) Co-fermentation of waste activated sludge with food waste for short-chain fatty acids production: effect of pH at ambient temperature. Front Environ Sci Eng China 5:623–632. https://doi.org/10.1007/s11783-011-0334-2

Fernández-Dacosta C, Posada JA, Kleerebezem R et al (2015) Microbial community-based polyhydroxyalkanoates (PHAs) production from wastewater: techno-economic analysis and ex-ante environmental assessment. Bioresour Technol 185:368–377. https://doi.org/10.1016/j.biortech.2015.03.025

Fu H, Sun Y, Teng H et al (2015) Salting-out extraction of carboxylic acids. Sep Purif Technol 139:36–42. https://doi.org/10.1016/j.seppur.2014.11.001

Fu H, Wang X, Sun Y et al (2017) Effects of salting-out and salting-out extraction on the separation of butyric acid. Sep Purif Technol 180:44–50. https://doi.org/10.1016/j.seppur.2017.02.042

Gao J, Chen L, Yuan K et al (2013) Ionic liquid pretreatment to enhance the anaerobic digestion of lignocellulosic biomass. Bioresour Technol 150:352–358. https://doi.org/10.1016/j.biortech.2013.10.026

Garcia-Aguirre J, Aymerich E, González-Mtnez de Goñi J, Esteban-Gutiérrez M (2017) Selective VFA production potential from organic waste streams: assessing temperature and pH influence. Bioresour Technol 244:1081–1088. https://doi.org/10.1016/j.biortech.2017.07.187

Gebrezgabher SA, Meuwissen MPM, Prins BAM, Lansink AGJMO (2010) Economic analysis of anaerobic digestion: a case of green power biogas plant in The Netherlands. NJAS Wageningen J Life Sci 57:109–115. https://doi.org/10.1016/j.njas.2009.07.006

Gerardi MH (2003) The microbiology of anaerobic digesters. Wiley, Hoboken

Goldberg AL (1972) Correlation between rates of degradation of bacterial proteins in vivo and their sensitivity to proteases. Proc Natl Acad Sci 69:2640–2644. https://doi.org/10.1073/pnas.69.9.2640

Gomes J, Frasson D, Quinta-Ferreira RM et al (2019) Removal of enteric pathogens from real wastewater using single and catalytic ozonation. Water (Switzerland) 11:1–12. https://doi.org/10.3390/w11010127

Greses S, Tomás-Pejó E, Gónzalez-Fernández C (2020) Agroindustrial waste as a resource for volatile fatty acids production via anaerobic fermentation. Bioresour Technol 297:122486. https://doi.org/10.1016/j.biortech.2019.122486

Guo P, Mochidzuki K, Cheng W et al (2011) Effects of different pretreatment strategies on corn stalk acidogenic fermentation using a microbial consortium. Bioresour Technol 102:7526–7531. https://doi.org/10.1016/j.biortech.2011.04.083

Guo W, Wu Q, Yang S et al (2014) Optimization of ultrasonic pretreatment and substrate/inoculum ratio to enhance hydrolysis and volatile fatty acid production from food waste. RSC Adv 4:53321–53326. https://doi.org/10.1039/C4RA08202H

Hobson PN, Wheatley AD (1994) Anaerobic digestion; modern theory and practice. Int J Biochem 26:856. https://doi.org/10.1016/0020-711X(94)90122-8

Hong C, Haiyun W (2010) Optimization of volatile fatty acid production with co-substrate of food wastes and dewatered excess sludge using response surface methodology. Bioresour Technol 101:5487–5493. https://doi.org/10.1016/j.biortech.2010.02.013

Hong S, Shirai Y, Aini ARN, Hassan M (2009) Semi-continuous and continuous anaerobic treatment of palm oil mill effluent for the production of organic acids and polyhydroxyalkanoates. Res J Environ Sci 3:552–559. https://doi.org/10.3923/rjes.2009.552.559

Hu Z-H, Yu H-Q, Zheng J-C (2006) Application of response surface methodology for optimization of acidogenesis of cattail by rumen cultures. Bioresour Technol 97:2103–2109. https://doi.org/10.1016/j.biortech.2005.09.025

Huang C, Xu T, Zhang Y et al (2007) Application of electrodialysis to the production of organic acids: state-of-the-art and recent developments. J Memb Sci 288:1–12. https://doi.org/10.1016/j.memsci.2006.11.026

Huang L, Chen Z, Xiong D et al (2018) Oriented acidification of wasted activated sludge (WAS) focused on odd-carbon volatile fatty acid (VFA): regulation strategy and microbial community dynamics. Water Res 142:256–266. https://doi.org/10.1016/j.watres.2018.05.062

Hussain A, Filiatrault M, Guiot SR (2017) Acidogenic digestion of food waste in a thermophilic leach bed reactor: effect of pH and leachate recirculation rate on hydrolysis and volatile fatty acid production. Bioresour Technol 245:1–9. https://doi.org/10.1016/j.biortech.2017.08.130

Iglesias-Iglesias R, Campanaro S, Treu L et al (2019) Valorization of sewage sludge for volatile fatty acids production and role of microbiome on acidogenic fermentation. Bioresour Technol 291:121817. https://doi.org/10.1016/j.biortech.2019.121817

Information National Center for Biotechnology (2018) PubChem compound database. https://pubchem.ncbi.nlm.nih.gov/. Accessed 25 April 2018

Izumi K, Okishio Y, Nagao N et al (2010) Effects of particle size on anaerobic digestion of food waste. Int Biodeterior

Biodegradation 64:601–608. https://doi.org/10.1016/j.ibiod.2010.06.013

Jankowska E, Duber A, Chwialkowska J et al (2018) Conversion of organic waste into volatile fatty acids: the influence of process operating parameters. Chem Eng J 345:395–403. https://doi.org/10.1016/j.cej.2018.03.180

Jayakrishnan U, Deka D, Das G (2019) Enhancing the volatile fatty acid production from agro-industrial waste streams through sludge pretreatment. Environ Sci Water Res Technol 5:334. https://doi.org/10.1039/c8ew00715b

Ji Z, Chen G, Chen Y (2010) Effects of waste activated sludge and surfactant addition on primary sludge hydrolysis and short-chain fatty acids accumulation. Bioresour Technol 101:3457–3462. https://doi.org/10.1016/j.biortech.2009.12.117

Jiang S, Chen Y, Zhou Q, Gu G (2007) Biological short-chain fatty acids (SCFAs) production from waste-activated sludge affected by surfactant. Water Res 41:3112–3120. https://doi.org/10.1016/j.watres.2007.03.039

Jiang S, Chen Y, Zhou Q (2007) Effect of sodium dodecyl sulfate on waste activated sludge hydrolysis and acidification. Chem Eng J 132:311–317. https://doi.org/10.1016/j.cej.2007.01.017

Jiang Y, Marang L, Tamis J et al (2012) Waste to resource: converting paper mill wastewater to bioplastic. Water Res 46:5517–5530. https://doi.org/10.1016/j.watres.2012.07.028

Jiang J, Zhang Y, Li K et al (2013) Volatile fatty acids production from food waste: effects of pH, temperature, and organic loading rate. Bioresour Technol 143:525–530. https://doi.org/10.1016/j.biortech.2013.06.025

Jones RJ, Massanet-Nicolau J, Guwy A et al (2015) Removal and recovery of inhibitory volatile fatty acids from mixed acid fermentations by conventional electrodialysis. Bioresour Technol 189:279–284. https://doi.org/10.1016/j.biortech.2015.04.001

Jones RJ, Massanet-Nicolau J, Mulder MJJ et al (2017) Increased biohydrogen yields, volatile fatty acid production and substrate utilisation rates via the electrodialysis of a continually fed sucrose fermenter. Bioresour Technol 229:46–52. https://doi.org/10.1016/j.biortech.2017.01.015

Jönsson LJ, Martín C (2016) Pretreatment of lignocellulose: formation of inhibitory by-products and strategies for minimizing their effects. Bioresour Technol 199:103–112. https://doi.org/10.1016/j.biortech.2015.10.009

Jung K, Choi J, Lee D et al (2015) Permeation characteristics of volatile fatty acids solution by forward osmosis. Process Biochem 50:669–677. https://doi.org/10.1016/j.procbio.2015.01.016

Kertes AS, King CJ, Blanch HW (2009) Extraction chemistry of fermentation product carboxylic acids. Biotechnol Bioeng 103:431–445. https://doi.org/10.1002/bit.22375

Kim HJ, Choi YG, Kim DY et al (2005) Effect of pretreatment on acid fermentation of organic solid waste. Water Sci Technol 52:153–160. https://doi.org/10.2166/wst.2005.0511

Kim HJ, Kim SH, Choi YG et al (2006) Effect of enzymatic pretreatment on acid fermentation of food waste. J Chem Technol Biotechnol 81:974–980. https://doi.org/10.1002/jctb.1484

Kleerebezem R, Joosse B, Rozendal R, Van Loosdrecht MCMM (2015) Anaerobic digestion without biogas? Rev Environ Sci Biotechnol 14:787–801. https://doi.org/10.1007/s11157-015-9374-6

Kumar AN, Mohan SV (2018) Acidogenic valorization of vegetable waste for short chain carboxylic acids and biohydrogen production: influence of pretreatment and pH. J Clean Prod 203:1055–1066. https://doi.org/10.1016/j.jclepro.2018.08.198

Kushkevych I, Kobzová E, Vítězová M et al (2019) Acetogenic microorganisms in operating biogas plants depending on substrate combinations. Biologia (Bratisl) 74:1229–1236. https://doi.org/10.2478/s11756-019-00283-2

Lee WS, Chua ASM, Yeoh HK, Ngoh GC (2014) A review of the production and applications of waste-derived volatile fatty acids. Chem Eng J 235:83–99. https://doi.org/10.1016/j.cej.2013.09.002

Li Y, Hua D, Zhang J et al (2013) Volatile fatty acids distribution during acidogenesis of algal residues with pH control. World J Microbiol Biotechnol 29:1067–1073. https://doi.org/10.1007/s11274-013-1270-z

Li X, Swan JE, Nair GR, Langdon AG (2015) Preparation of volatile fatty acid (VFA) calcium salts by anaerobic digestion of glucose. Biotechnol Appl Biochem 62:476–482. https://doi.org/10.1002/bab.1301

Li X, Zhao J, Wang D et al (2016) An efficient and green pretreatment to stimulate short-chain fatty acids production from waste activated sludge anaerobic fermentation using free nitrous acid. Chemosphere. https://doi.org/10.1016/j.chemosphere.2015.08.076

Li Y, Zhang X, Xu H et al (2019) Acidogenic properties of carbohydrate-rich wasted potato and microbial community analysis: effect of pH. J Biosci Bioeng 128:50–55. https://doi.org/10.1016/j.jbiosc.2018.12.009

Lim S-J, Choi DW, Lee WG et al (2000) Volatile fatty acids production from food wastes and its application to biological nutrient removal. Bioprocess Eng 22:543–545. https://doi.org/10.1007/s004499900109

Lim S-J, Kim BJ, Jeong C-M et al (2008) Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor. Bioresour Technol 99:7866–7874. https://doi.org/10.1016/j.biortech.2007.06.028

Lin L, Li R, Li X (2018) Recovery of organic resources from sewage sludge of Al-enhanced primary sedimentation by alkali pretreatment and acidogenic fermentation. J Clean Prod 172:3334–3341. https://doi.org/10.1016/j.jclepro.2017.11.199

Liotta F, D'Antonio G, Esposito G et al (2014) Effect of total solids content on methane and volatile fatty acid production in anaerobic digestion of food waste. Waste Manag Res 32:947–953. https://doi.org/10.1177/0734242X14550740

Liu N, Wang Q, Jiang J, Zhang H (2017) Effects of salt and oil concentrations on volatile fatty acid generation in food waste fermentation. Renew Energy 113:1523–1528. https://doi.org/10.1016/j.renene.2017.07.042

Liu N, Jiang J, Yan F et al (2018) Optimization of simultaneous production of volatile fatty acids and bio-hydrogen from food waste using response surface methodology. RSC Adv 8:10457–10464. https://doi.org/10.1039/C7RA13268A

Liu H, Han P, Liu H et al (2018) Full-scale production of VFAs from sewage sludge by anaerobic alkaline fermentation to improve biological nutrients removal in domestic wastewater. Bioresour Technol 260:105–114. https://doi.org/10.1016/j.biortech.2018.03.105

Lone SA, Raghunathan S, Davoodbasha MA et al (2019) An investigation on the sterilization of berry fruit using ozone: an option to preservation and long-term storage. Biocatal Agric Biotechnol. https://doi.org/10.1016/j.bcab.2019.101212

Longo S, Katsou E, Malamis S et al (2015) Recovery of volatile fatty acids from fermentation of sewage sludge in municipal wastewater treatment plants. Bioresour Technol 175:436–444. https://doi.org/10.1016/j.biortech.2014.09.107

López-Garzón CS, Straathof AJJ (2014) Recovery of carboxylic acids produced by fermentation. Biotechnol Adv 32:873–904. https://doi.org/10.1016/j.biotechadv.2014.04.002

Ma H, Liu H, Zhang L et al (2017) Novel insight into the relationship between organic substrate composition and volatile fatty acids distribution in acidogenic co-fermentation. Biotechnol Biofuels 10:137. https://doi.org/10.1186/s13068-017-0821-1

Magdalena JA, Tomás-Pejó E, Ballesteros M, González-Fernandez C (2018) Volatile fatty acids production from protease pretreated *Chlorella* biomass via anaerobic digestion. Biotechnol Prog. https://doi.org/10.1002/btpr.2696

Maharaj I, Elefsiniotis P (2001) The role of HRT and low temperature on the acid-phase anaerobic digestion of municipal and industrial wastewaters. Bioresour Technol 76:191–197. https://doi.org/10.1016/S0960-8524(00)00128-0

Mata-Alvarez J, Macé S, Llabrés P (2000) Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. Bioresour Technol 74:3–16. https://doi.org/10.1016/S0960-8524(00)00023-7

Mato T, Ben M, Kennes C, Veiga MC (2010) Valuable product production from wood mill effluents. Water Sci Technol 62:2294. https://doi.org/10.2166/wst.2010.949

Matsakas L, Gao Q, Jansson S et al (2017) Green conversion of municipal solid wastes into fuels and chemicals. Electron J Biotechnol 26:69–83. https://doi.org/10.1016/j.ejbt.2017.01.004

Mengmeng C, Hong C, Qingliang Z et al (2009) Optimal production of polyhydroxyalkanoates (PHA) in activated sludge fed by volatile fatty acids (VFAs) generated from alkaline excess sludge fermentation. Bioresour Technol 100:1399–1405. https://doi.org/10.1016/j.biortech.2008.09.014

Min K, Khan A, Kwon M et al (2005) Acidogenic fermentation of blended food-waste in combination with primary sludge for the production of volatile fatty acids. J Chem Technol Biotechnol 80:909–915. https://doi.org/10.1002/jctb.1261

Mostafa NA (1999) Production and recovery of volatile fatty acids from fermentation broth. Energy Convers Manag 40:1543–1553. https://doi.org/10.1016/S0196-8904(99)00043-6

Mumtaz T, Abd-Aziz S, Rahman NA et al (2008) Pilot-scale recovery of low molecular weight organic acids from anaerobically treated palm oil mill effluent (POME) with energy integrated system. African J Biotechnol 7:3900–3905. https://doi.org/10.5897/AJB08.640

Odnell A, Recktenwald M, Stensén K et al (2016) Activity, life time and effect of hydrolytic enzymes for enhanced biogas production from sludge anaerobic digestion. Water Res 103:462–471. https://doi.org/10.1016/j.watres.2016.07.064

Oktem YA, Ince O, Donnelly T et al (2006) Determination of optimum operating conditions of an acidification reactor treating a chemical synthesis-based pharmaceutical wastewater. Process Biochem 41:2258–2263. https://doi.org/10.1016/j.procbio.2006.05.016

Omar FN, Rahman NAA, Hafid HS et al (2009) Separation and recovery of organic acids from fermented kitchen waste by an integrated process. Afr J Biotechnol 8:5807–5813. https://doi.org/10.5897/AJB09.992

Outram V, Ramos Suarez M (2020) Prinicipal component analysis of acidiogenic fermentation. https://doi.org/10.6084/m9.figshare.11854857

Outram V, Zhang Y (2018) Solvent-free membrane extraction of volatile fatty acids from acidogenic fermentation. Bioresour Technol 270:400–408. https://doi.org/10.1016/j.biortech.2018.09.057

Ozkan L, Erguder TH, Demirer GN (2011) Effects of pretreatment methods on solubilization of beet-pulp and bio-hydrogen production yield. Int J Hydrogen Energy 36:382–389. https://doi.org/10.1016/j.ijhydene.2010.10.006

Pan X-R, Li W-W, Huang L et al (2018) Recovery of high-concentration volatile fatty acids from wastewater using an acidogenesis-electrodialysis integrated system. Bioresour Technol 260:61–67. https://doi.org/10.1016/j.biortech.2018.03.083

Pant D, Arslan D, Van Bogaert G et al (2013) Integrated conversion of food waste diluted with sewage into volatile fatty acids through fermentation and electricity through a fuel cell. Environ Technol 34:1935–1945. https://doi.org/10.1080/09593330.2013.828763

Paul S, Dutta A (2018) Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. Resour Conserv Recycl 130:164–174. https://doi.org/10.1016/j.resconrec.2017.12.005

Pellera F-M, Santori S, Pomi R et al (2016) Effect of alkaline pretreatment on anaerobic digestion of olive mill solid waste. Waste Manag 58:160–168. https://doi.org/10.1016/j.wasman.2016.08.008

Plácido J, Zhang Y (2018) Evaluation of esterification and membrane based solvent extraction as methods for the recovery of short chain volatile fatty acids from slaughterhouse blood anaerobic mixed fermentation. Waste Biomass Valorization 9:1767–1777. https://doi.org/10.1007/s12649-017-9952-7

Plácido J, Zhang Y (2018) Production of volatile fatty acids from slaughterhouse blood by mixed-culture fermentation. Biomass Convers Biorefinery 8:621–634. https://doi.org/10.1007/s13399-018-0313-y

Rahmani AR, Shabanloo A, Mehralipou J et al (2015) Degradation of phenol in aqueous solutions using electro-fenton process. Res J Environ Sci 9:332–341. https://doi.org/10.3923/rjes.2015.332.341

Rebecchi S, Pinelli D, Bertin L et al (2016) Volatile fatty acids recovery from the effluent of an acidogenic digestion process fed with grape pomace by adsorption on ion exchange resins. Chem Eng J 306:629–639. https://doi.org/10.1016/j.cej.2016.07.101

Reyhanitash E, Zaalberg B, Kersten SRA, Schuur B (2016) Extraction of volatile fatty acids from fermented wastewater. Sep Purif Technol 161:61–68. https://doi.org/10.1016/j.seppur.2016.01.037

Reyhanitash E, Kersten SRA, Schuur B (2017) Recovery of volatile fatty acids from fermented wastewater by adsorption. ACS Sustain Chem Eng 5:9176–9184. https://doi.org/10.1021/acssuschemeng.7b02095

Reyhanitash E, Brouwer T, Kersten SRA et al (2018) Liquid–liquid extraction-based process concepts for recovery of carboxylic acids from aqueous streams evaluated for dilute streams. Chem Eng Res Des 137:510–533. https://doi.org/10.1016/j.cherd.2018.07.038

Reyhanitash E, Fufachev E, Van Munster KD et al (2019) Recovery and conversion of acetic acid from a phosphonium phosphinate ionic liquid to enable valorization of fermented wastewater. Green Chem 21:2023–2034. https://doi.org/10.1039/c9gc00725c

Rocha MAA, Raeissi S, Hage P et al (2017) Recovery of volatile fatty acids from water using medium-chain fatty acids and a cosolvent. Chem Eng Sci 165:74–80. https://doi.org/10.1016/j.ces.2017.02.014

Romero-Cedillo L, Poggi-Varaldo HM, Ponce-Noyola T et al (2017) A review of the potential of pretreated solids to improve gas biofuels production in the context of an OFMSW biorefinery. J Chem Technol Biotechnol 92:937–958. https://doi.org/10.1002/jctb.5116

Rosen Y, Mamane H, Gerchman Y (2019) Short ozonation of lignocellulosic waste as energetically favorable pretreatment. Bioenergy Res 12:292–301. https://doi.org/10.1007/s12155-019-9962-3

Rulli MC, Bellomi D, Cazzoli A et al (2016) The water-land-food nexus of first-generation biofuels OPEN. Nat Publ Gr. https://doi.org/10.1038/srep22521

Sans C, Mata-Alvarez J, Cecchi F et al (1995) Acidogenic fermentation of organic urban wastes in a plug-flow reactor under thermophilic conditions. Bioresour Technol 54:105–110. https://doi.org/10.1016/0960-8524(95)00098-4

Sans C, Mata-Alvarez J, Cecchi F et al (1995) Volatile fatty acids production by mesophilic fermentation of mechanically-sorted urban organic wastes in a plug-flow reactor. Bioresour Technol 51:89–96. https://doi.org/10.1016/0960-8524(95)95866-Z

Sarkar O, Venkata Mohan S (2017) Pre-aeration of food waste to augment acidogenic process at higher organic load: valorizing biohydrogen, volatile fatty acids and biohythane. Bioresour Technol 242:68–76. https://doi.org/10.1016/j.biortech.2017.05.053

Schlosser Š, Kertész R, Marták J (2005) Recovery and separation of organic acids by membrane-based solvent extraction and pertraction. Sep Purif Technol 41:237–266. https://doi.org/10.1016/j.seppur.2004.07.019

Scoma A, Varela-Corredor F, Bertin L et al (2016) Recovery of VFAs from anaerobic digestion of dephenolized olive mill wastewaters by electrodialysis. Sep Purif Technol 159:81–91. https://doi.org/10.1016/j.seppur.2015.12.029

Shen D, Yin J, Yu X et al (2017) Acidogenic fermentation characteristics of different types of protein-rich substrates in food waste to produce volatile fatty acids. Bioresour Technol 227:125–132. https://doi.org/10.1016/j.biortech.2016.12.048

Silva FC, Serafim LS, Nadais H et al (2013) Acidogenic fermentation towards valorisation of organic waste streams into volatile fatty acids. Chem Biochem Eng Q 27:467–476

Smyth BM, Smyth H, Murphy JD (2010) Can grass biomethane be an economically viable biofuel for the farmer and the consumer? Biofuels, Bioprod Biorefining 4:519–537. https://doi.org/10.1002/bbb.238

Solichien MS, O'Brien D, Hammond EG, Glatz CE (1995) Membrane-based extractive fermentation to produce propionic and acetic acids: toxicity and mass transfer considerations. Enzyme Microb Technol 17:23–31. https://doi.org/10.1016/0141-0229(94)00086-7

Straathof AJJ (2014) Transformation of biomass into commodity chemicals using enzymes or cells. Chem Rev 114:1871–1908. https://doi.org/10.1021/cr400309c

Tampio EA, Blasco L, Vainio MM et al (2018) Volatile fatty acids (VFAs) and methane from food waste and cow slurry: comparison of biogas and VFA fermentation processes. GCB Bioenergy 11:72–84. https://doi.org/10.1111/gcbb.12556

Tao B, Passanha P, Kumi P et al (2016) Recovery and concentration of thermally hydrolysed waste activated sludge derived volatile fatty acids and nutrients by microfiltration, electrodialysis and struvite precipitation for polyhydroxyalkanoates production. Chem Eng J 295:11–19. https://doi.org/10.1016/j.cej.2016.03.036

Tao B, Alessi AM, Zhang Y et al (2019) Simultaneous biomethanisation of endogenous and imported CO_2 in organically loaded anaerobic digesters. Appl Energy 247:670–681. https://doi.org/10.1016/j.apenergy.2019.04.058

Trad Z, Akimbomi J, Vial C et al (2015) Development of a submerged anaerobic membrane bioreactor for concurrent extraction of volatile fatty acids and biohydrogen production. Bioresour Technol 196:290–300. https://doi.org/10.1016/j.biortech.2015.07.095

Travaini R, Martín-Juárez J, Lorenzo-Hernando A, Bolado-Rodríguez S (2016) Ozonolysis: an advantageous pretreatment for lignocellulosic biomass revisited. Bioresour Technol 199:2–12. https://doi.org/10.1016/j.biortech.2015.08.143

Tugtas AE (2014) Recovery of volatile fatty acids via membrane contactor using flat membranes: experimental and theoretical analysis. Waste Manag 34:1171–1178. https://doi.org/10.1016/j.wasman.2014.01.020

United States Environmental Protection Agency (2016) Chemical reporting data under the toxic substances control act. https://www.epa.gov/chemical-data-reporting. Accessed 4 May 2018

Uyar B, Eroglu I, Yücel M, Gündüz U (2009) Photofermentative hydrogen production from volatile fatty acids present in dark fermentation effluents. Int J Hydrogen Energy 34:4517–4523. https://doi.org/10.1016/j.ijhydene.2008.07.057

Vajda M, Sabolová E, Schlosser Š, Mikulová E (2003) Membrane-based extraction joined with membrane-based stripping in a circulating arrangement II. Extraction of organic acids Chem Pap 57:3–10

Veeken A, Kalyuzhnyi S, Scharff H, Hamelers B (2000) Effect of pH and VFA on hydrolysis of organic solid waste. J Environ Eng. https://doi.org/10.1061/(ASCE)0733-9372(2000)126

Wainaina S, Kumar Awasthi M, Taherzadeh MJ (2019) Bioengineering of anaerobic digestion for volatile fatty acids, hydrogen or methane production: a critical review. Bioengineered 10:437–458. https://doi.org/10.1080/21655979.2019.1673937

Wallis C, Cerny M, Lacroux E, Mouloungui Z (2017) Recovery of slaughterhouse animal fatty wastewater sludge by conversion into fatty acid butyl esters by acid-catalyzed esterification. Waste Manag 60:184–190. https://doi.org/10.1016/j.wasman.2016.07.003

Wang K, Yin J, Shen D, Li N (2014) Anaerobic digestion of food waste for volatile fatty acids (VFAs) production with different types of inoculum: effect of pH. Bioresour Technol 161:395–401. https://doi.org/10.1016/j.biortech.2014.03.088

Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85:849–860. https://doi.org/10.1007/s00253-009-2246-7

Wu H, Yang D, Zhou Q, Song Z (2009) The effect of pH on anaerobic fermentation of primary sludge at room temperature. J Hazard Mater 172:196–201. https://doi.org/10.1016/j.jhazmat.2009.06.146

Wu Q, Guo W, Yang S et al (2015) Enhancement of volatile fatty acid production using semi-continuous anaerobic food waste fermentation without pH control. RSC Adv 5:103876–103883. https://doi.org/10.1039/C5RA21162J

Wu Q, Guo W, Yang S et al (2015) Effects of ultrasonic and acid pretreatment on food waste disintegration and volatile fatty acid production. J Harbin Inst Technol. https://doi.org/10.11916/j.issn.1005-9113.2015.03.001

Wu L, Zhang C, Hu H et al (2017) Phosphorus and short-chain fatty acids recovery from waste activated sludge by anaerobic fermentation: effect of acid or alkali pretreatment. Bioresour Technol. https://doi.org/10.1016/j.biortech.2017.03.016

Xin X, He J, Qiu W (2018) Volatile fatty acid augmentation and microbial community responses in anaerobic co-fermentation process of waste-activated sludge mixed with corn stalk and livestock manure. Environ Sci Pollut Res 25:4846–4857. https://doi.org/10.1007/s11356-017-0834-0

Xiong B, Richard TL, Kumar M (2015) Integrated acidogenic digestion and carboxylic acid separation by nanofiltration membranes for the lignocellulosic carboxylate platform. J Memb Sci 489:275–283. https://doi.org/10.1016/j.memsci.2015.04.022

Yan L, Sun YQ, Wang XD et al (2018) Partition behavior of monocarboxylic acids in salting-out extraction systems of monohydric alcohols and dipotassium phosphate. Sep Purif Technol 199:351–358. https://doi.org/10.1016/j.seppur.2018.02.006

Yang G, Wang J (2017) Fermentative hydrogen production from sewage sludge. Crit Rev Environ Sci Technol. https://doi.org/10.1080/10643389.2017.1348107

Yeneneh AM, Chong S, Sen TK et al (2013) Effect of ultrasonic, microwave and combined microwave–ultrasonic pretreatment of municipal sludge on anaerobic digester performance. Water Air Soil Pollut 224:1559. https://doi.org/10.1007/s11270-013-1559-4

Yesil H, Tugtas AE, Bayrakdar A, Calli B (2014) Anaerobic fermentation of organic solid wastes: volatile fatty acid production and separation. Water Sci Technol 69:2132. https://doi.org/10.2166/wst.2014.132

Yesil H, Taner H, Ugur Nigiz F et al (2018) Pervaporative separation of mixed volatile fatty acids: a study towards integrated VFA production and separation. Waste Biomass Valorization. https://doi.org/10.1007/s12649-018-0504-6

Yin J, Wang K, Yang Y et al (2014) Improving production of volatile fatty acids from food waste fermentation by hydrothermal pretreatment. Bioresour Technol 171:323–329. https://doi.org/10.1016/j.biortech.2014.08.062

Yin J, Yu X, Zhang Y et al (2016) Enhancement of acidogenic fermentation for volatile fatty acid production from food waste: effect of redox potential and inoculum. Bioresour Technol 216:996–1003. https://doi.org/10.1016/j.biortech.2016.06.053

Yirong C, Heaven S, Banks CJ (2015) Effect of a trace element addition strategy on volatile fatty acid accumulation in thermophilic anaerobic digestion of food waste. Waste Biomass Valorization 6:1–12. https://doi.org/10.1007/s12649-014-9327-2

Yousuf A, Bonk F, Bastidas-Oyanedel J-R, Schmidt JE (2016) Recovery of carboxylic acids produced during dark fermentation of food waste by adsorption on Amberlite IRA-67 and activated carbon. Bioresour Technol 217:137–140. https://doi.org/10.1016/j.biortech.2016.02.035

Yu HQ, Fang HHP (2000) Thermophilic acidification of dairy wastewater. Appl Microbiol Biotechnol 54:439–444. https://doi.org/10.1007/s002530000390

Yu HQ, Fang HHP (2001) Acidification of mid- and high-strength dairy wastewaters. Water Res 35:3697–3705. https://doi.org/10.1016/S0043-1354(01)00077-X

Yu HQ, Fang HHP (2003) Acidogenesis of gelatin-rich wastewater in an upflow anaerobic reactor: influence of pH and temperature. Water Res 37:55–66. https://doi.org/10.1016/S0043-1354(02)00256-7

Yu X, Yin J, Wang K et al (2016) Enhancing food waste hydrolysis and the production rate of volatile fatty acids by prefermentation and hydrothermal pretreatments. Energy Fuels 30:4002–4008. https://doi.org/10.1021/acs.energyfuels.6b00077

Yue L, Cheng J, Hua J et al (2019) Improving fermentative methane production of glycerol trioleate and food waste pretreated with ozone through two-stage dark hydrogen fermentation and anaerobic digestion. Energy Convers Manag. https://doi.org/10.1016/j.enconman.2019.112225

Zacharof M-P, Lovitt RW (2014) Recovery of volatile fatty acids (VFA) from complex waste effluents using membranes. Water Sci Technol 69:495–503. https://doi.org/10.2166/wst.2013.717

Zacharof M-P, Mandale SJ, Williams PM, Lovitt RW (2016) Nanofiltration of treated digested agricultural wastewater for recovery of carboxylic acids. J Clean Prod 112:4749–4761. https://doi.org/10.1016/j.jclepro.2015.07.004

Zhang Y, Angelidaki I (2015) Bioelectrochemical recovery of waste-derived volatile fatty acids and production of hydrogen and alkali. Water Res 81:188–195. https://doi.org/10.1016/j.watres.2015.05.058

Zhang B, Zhang L-L, Zhang S-C et al (2005) The influence of pH on hydrolysis and acidogenesis of kitchen wastes in two-phase anaerobic digestion. Environ Technol 26:329–340. https://doi.org/10.1080/09593332608618563

Zhang P, Chen Y, Zhou Q (2009) Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: effect of pH. Water Res 43:3735–3742. https://doi.org/10.1016/j.watres.2009.05.036

Zhang Z, Li W, Zhang G, Xu G (2014) Impact of pretreatment on solid state anaerobic digestion of yard waste for biogas production. World J Microbiol Biotechnol 30:547–554. https://doi.org/10.1007/s11274-013-1473-3

Zhang R, Liu F, Liu H, Zhang D (2017) Pretreatment of corn with diluted nitric acid for the enhancement of acidogenic fermentation. https://doi.org/10.1021/acs.energyfuels.7b02596

Zhang L, Loh KC, Dai Y, Tong YW (2020) Acidogenic fermentation of food waste for production of volatile fatty acids: bacterial community analysis and semi-continuous operation. Waste Manag 109:75–84. https://doi.org/10.1016/j.wasman.2020.04.052

Zhou A, Yang C, Kong F et al (2013) Improving the short-chain fatty acids production of waste activated sludge stimulated by a bi-frequency ultrasonic pretreatment. J Environ Biol 34:381–389