Expanding the Anaerobic Digestion Map: A Review of Intermediates in the Digestion of Food Waste

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Abstract

Anaerobic digestion is a promising technology as a renewable source of energy products, but these products have low economic value and process control is challenging. Identifying intermediates formed throughout the process could enhance understanding and offer opportunities for improved monitoring, control, and valorisation. In this review, intermediates present in the anaerobic digestion process are identified and discussed, including the following: VFAs, carboxylic acid, amino acids, furans, terpenes and phytochemicals. The key limitations associated with exploiting these intermediates are also addressed including challenging mixed cultures of microbiology, complex feedstocks, and difficult extraction and separation techniques.

Keywords: AD, model, valorization, optimisation, product

1. Introduction

Approximately 9.5 million tonnes of food waste are generated annually (post farm gate) in the UK alone (30% inedible) (WRAP, 2020). If sent to unmanaged landfill, the greenhouse gases produced as the organic matter breaks down are released to the atmosphere and contribute to climate change. WRAP estimates that 25 million tonnes of greenhouse gases are generated from food waste in the UK alone (WRAP, 2020). Whilst some of this waste can be avoided, finding alternate uses for those which cannot is critical for reducing carbon footprint. By capturing food waste and controlling this process through anaerobic digestion (AD), there exists an opportunity to extract commercially viable and sustainable products.

AD is an effective technology in the valorisation of food waste (Carmona-Cabello et al., 2018; Cristóbal et al., 2018; Dahiya et al., 2018). Frequently incorporated into biorefinery approaches, AD converts waste streams to biofuels (Gupta et al., 2014) in the following stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Carmona-Cabello et al., 2018; Mateescu and Constantinescu, 2011). During this process, AD passes through a series of intermediates and potential products.

Early models of AD identified several important intermediates in the AD process. Andrews and Graef (1971) and McCarty (1964) recognised the importance of VFAs and this was extended to include general organics (Hill and Barth, 1977) and glucose (Costello et al., 1991). Angelidaki et al (1999) proposed a generally applicable model which established a map of AD intermediates. This model separates the substrate into carbohydrates, proteins and lipid, and includes long chain fatty acids (LCFA), glycerol and amino acids as

intermediates. In addition, VFAs, were represented individually as acetic, propionic, butyric and valeric acid (Angelidaki et al., 1999). The current industry standard for AD modelling is the Anaerobic Digestion Model 1 (ADM1) developed by the International Water Association (IWA). This model follows the general structure proposed by Angelidaki et al (1999) and was designed to maximise applicability, whilst maintaining simplicity (Batstone and Angelidaki, 2014), therefore many other known intermediates are not included.

Many researchers have explored alternative products for the valorisation of food waste, such as; biofuels (biobutanol, bioethanol, biodiesel, biohydrogen, biomethane and biohytane) as well as bioactive molecules, carboxylic acids, furans and phytochemicals (such as phenolics and flavonoids) (Diaz et al., 2018; Fermoso et al., 2018; Galanakis, 2012; Koutinas et al., 2014; Kumar and Longhurst, 2018; Lin et al., 2014; Nazzaro et al., 2018; Ravindran and Jaiswal, 2016a; RedCorn et al., 2018; Waqas et al., 2018). Such intermediates, however, are not generally included in AD process maps. Use of the digestate by-product as a biofertiliser is also well established (DEFRA, 2011; Du et al., 2018), although this has not been discussed in this review. Research generally focuses on energy products (biogas/biofuels), exploring the other intermediates of AD, however, could reveal opportunities for alternative products or optimisation techniques.

Enhanced understanding of metabolic routes in the digestor would allow users to predict system performance, manipulate systems towards new products or to increase yield. Monitoring novel intermediate levels and understanding how their presence impacts AD, including inhibitory effects, could supplement existing optimisation techniques. Technology could also be introduced to extract high-value products under optimal conditions. This approach does, however, face several challenges such as complex mixed

cultures of microbiology, complex feedstocks, low yields, and extraction and separation techniques.

This review will focus on reported or speculative intermediates of interest produced through anaerobic, biological processes to present the potential opportunities for AD and existing research in these areas. The paper starts with an overview of the study methodology, then provides a brief bibliometric analysis of intermediates followed by a discussion of key examples from these groups. Finally, the challenges and limitations are summarised.

2. Methodology

An online search of scientific manuscripts was conducted using ScienceDirect and Web of Science. As no previous reviews were identified exploring intermediates of AD a wide time frame was assumed (2000-2019). An initial search using the keywords 'food waste products' was used to identify review papers which evaluated all potential products from food waste and a list was compiled (Table 1), excluding any which are not naturally occurring within AD

To identify studies which reported the presence of these molecules during AD a further search was conducted using a Boolean search containing the intermediate name and keywords 'anaerobic digestion' or 'anaerobic fermentation'. Bibliometric analysis of this was compiled to identify general trends. Papers were subsequently screened to identify those where the molecule was analysed as an intermediate or in the final product (as opposed to present in the substrate). Where significant numbers of papers were identified (in the case of biogas and biofuels), relevant review papers and recent developments (2015-2020) were

selected. In total 118 manuscripts were included in this review. Prominent examples are discussed in section **Error! Reference source not found.**.

3. Anaerobic Digestion Intermediates

Intermediates are presented in the groups shown in Table 1 with key examples discussed. Figure 1 shows an extended map of the AD process, including the intermediates discussed in this review.

3.1. Bibliometric Analysis

Bibliometric analysis (Figure 2) of intermediates over the last 20 years indicates a general increasing research trend. While some of this is expected (sugars and amino acids generally correlate with the increase in biogas research), other increases are more interesting; the rise in phenolics or carboxylic acids research for example. This points towards a general interest in broadening the knowledge of AD and its intermediates.

3.2. Methanogenesis Products

Production of biogas from food waste is well studied in the literature (Braguglia et al., 2018; Mao et al., 2015; Ren et al., 2018) and therefore will only be discussed in brief here. Methane-based biogas production is one of the most robust applications of AD and food waste. In addition, poor water solubility of the methane results in natural separation of the product, limiting any downstream processing requirements (Kleerebezem et al., 2015). The biogas is used as an energy source and acts as a sustainable alternative to fossil fuels (Dahiya et al., 2018). With the European biogas market estimated at $3 billion in 2018 (Gupta and Aditya Singh, 2019), valorising food waste through AD seems an attractive prospect. Biogas is, however, a relatively low-value product per atom with 1 m^3 required to

produce approximately 6.7 kWh of energy (NNFCC, n.d.) therefore economy of scale and cost minimisation are crucial to commerciality.

Production of methane requires the activity of methanogens which are known to be slow-growing and sensitive to environmental factors, such as pH (Mateescu and Constantinescu, 2011). *Methanobacterium*, *Methanococcus*, *Methanobrevibacter*, *Methanomicrobium*, M*ethanosarcina* and *Methanoseata* are reported as being the dominant methanogens (P. Wang et al., 2018).

3.3. Acetogenesis Products

Intermediates formed during acetogenesis are generally the result of reduction of organic acids, forming acetate and hydrogen. Biofuels, such as biohydrogen and biohythane (a mixture of methane and hydrogen (1:4)) have also been considered as a clean fuel with good calorific efficiency (Dahiya et al., 2018) and can also be used as a feedstock for the chemical synthesis (ammonia and nitrogen) (Nayak and Bhushan, 2019). Production of biohydrogen still faces challenges on an industrial scale owing to poor process control, storage and transportation (Khan et al., 2018). Studies have indicated that *Enterobacter*, *Bacillus*, *Clostridium* and *Thermotoga* are the genera primarily responsible for the production of biohydrogen (Nayak and Bhushan, 2019). During this process, the hydrogenotrophic group of methanogens are suppressed to ensure maximum production (Khan et al., 2018).

3.4. Acidogenesis Products

3.4.1. Biofuels

Production of alcohol-based biofuels takes place during acidogenesis and solventogenesis. Acetone, butanol and ethanol (ABE) fermentation (Hegde et al., 2018) produces industrial 1-

butanol (Ujor et al., 2014) or ethanol, common applications of which include transport and production of plastics (Nayak and Bhushan, 2019). The Renewable Fuels Association report approximately 100,000 L of fuel ethanol manufactured globally in 2018 (Renewable Fuels Association, 2019). Production of ethanol by fermentation can be achieved from a range of substrates, including starchy crops and lignocellulosic materials with *Saccharomyces cerevisiae* and *Zymomonas mobilis* two of the most well-known producers (Koutinas et al., 2014). Additionally, the use of *Clostridium* strains, including *Clostridium beijerinckii* (Ujor et al., 2014) or *Clostridium acetobutylicum* (Zhou et al., 2018) has proved effective for ABE fermentation. The route to product proceeds from glucose to acetyl-CoA then to acetoacetyl-CoA and finally to acetone or butanol, resulting in a 3:6:1 mixture (Zhou et al., 2018). Methanol, propanol, and iso-butanol have also been considered as a fuel source to a much lesser extent (Hegde et al., 2018).

3.4.2. Volatile Fatty Acids

Volatile fatty acids (VFAs) such as acetic, propionic, butyric and valeric are increasingly explored as alternative products of AD of food waste (Khan et al., 2016). VFAs offer a feasible valorisation of food waste using AD as precursors to biopolymers and other valuable products (Shen et al., 2017). Market value and demand for individual VFAs are illustrated in Table 2. As such, extraction of acids during the digestion process, though a technical challenge, could offer an economic advantage compared to biogas and, additionally, facilitates complete fermentation (Calt, 2015).

The production of VFAs through acidogenic fermentation has been documented via several metabolic pathways during AD, therefore the ratios of these acids in the final product mixture can vary. These pathways are classified as the following types: acetate-

ethanol type, propionate-type, butyrate-type and mixed acid with pyruvate being the critical point at which these pathways can deviate resulting in varying concentrations of products. The proportion of pyruvate processed by each of these pathways depends on the following conditions: substrate, environment and strains present in the inoculum (Zhou et al., 2018).

Mixed acid fermentation simultaneously produces acetate, propionate, butyrate and valerate. Key influencing factors include substrates, pH and redox potential as well as inoculum bacteria and enzyme production (Zhou et al., 2018). These waste-derived VFAs (acetic, propionic and butyric acid) are a promising substrate for the production of polyhydroxyalkanoates (biodegradable polymers) and bioenergy/biogas (Lee et al., 2014).

Alternatively, acetate-ethanol type, proportionate-type and butyrate-type pathways favourably produce more of the individual acids (acetic, propionic and butyric acid respectively). Many homoacetogenic anaerobes can produce acetic acid during fermentation of sugars and lactic acid, including *Clostridium formicoacetium*, *Moorella thermoacetica, Clostridium thermoaceticum*, *Clostridium aceticum*, *Acetobacterium woodii* and *Acetogenium kivui* (Scheper, 2016). Acetic acid production has also been linked to *Bifidobacteria*, which favours a pH of 4.5 (Feng et al., 2018) and it is also noted to be the dominant VFA product up to pH 5.5 for AD of landfill leachate (Begum et al., 2018). Similarly, *Propionibacterium* is responsible for the anaerobic production of propionic acid with the most common bacteria being *Propionibacterium acidipropionici*, *Propionibacterium freudenreichii*, *Propionibacterium shermanii* (Scheper, 2016) and are growth inhibited by the propionic acid presence due to the change in pH gradient (Koutinas et al., 2014). Propionate type metabolism employs two distinct pathways. In the first pyruvate is reduced to give lactate as an intermediate then to propionate. In the second acidogenic bacteria such as

Corynebacterium, *Propionibacterium* and *Bifidobacterium* produce proportionate via transcarboxylase cycle (Zhou et al., 2018).

Production of butyric acid through mixed acid fermentation is well documented with optimal conditions reported for pH (6-6.5) (Lee et al., 2014) and temperature (55˚C) (Zhou et al., 2018). Production can be achieved from glucose, xylose, fructose, glycerol, lignocellulosic materials, molasses, potato starch and cheese whey by any of the following microorganisms: *Clostridium*, *Butyrivibrio*, *Butyribacterium*, *Eubacterium*, *Fusobacterium*, *Megasphaera*, *Fusobacterium*, *Roseburia* and *Coprococcus*. *Clostridium tyrobutyricum* and *Clostridium butyricium* are the most well studied (Jiang et al., 2018; Koutinas et al., 2014; Scheper, 2016). Butyrate type metabolic pathways produce butyrate by reduction and decarboxylation of pyruvate with the consumption of acetate via acetyl-CoA, acetoacetyl-CoA, 3-hydroxybutryl-CoA, crotonyl-CoA and butyryl-CoA (Zhou et al., 2018). Similarly, isobutyric acid is a reported product of AD of hemicellulose and is a contributing factor to low pH and thus methanogenesis inhibition (W. Li et al., 2018).

3.4.3. Carboxylic Acids

Medium chain carboxylic acids (MCCAs) (comprised of 6-10 carbon chains) have been increasingly studied as products of AD. These acids are biologically synthesised via the reverse β-oxidation pathway, elongating VFAs by two carbons per cycle. This proceeds by the metabolic pathway via *Clostridium kluyveri* (Dahiya et al., 2018; De Groof et al., 2019) which has the unique ability to oxidise ethanol and couple it to other fermentation products, allowing it to produce these longer chain fatty acids (Madigan et al., 2009). Chain elongation has also been reported by *Megasphaera elsdenii* and *Ruminococcaceae* via lactic acid (De Groof et al., 2019). A two-stage hexanoic acid fermentation from fruit and

vegetable waste was reported by Yu et al. with the dominating microorganism being *Clostridium kluyveri* (Yu et al., 2019).

3.4.4. Hydroxycarboxylic Acids

Hydroxycarboxylic acid is a particularly significant intermediate in waste fermentation, which can become dominated by lactic acid production at low pH (3.2-4.5) (Feng et al., 2018). The global market for lactic acid was reported to be approximately 400,000 tonnes in 2016 (Scheper, 2016) and it has wide-ranging applications in food, chemical, cosmetic and pharmaceutical industries (Kumar and Longhurst, 2018) as a flavour enhancer, acidulant and preservative (Waqas et al., 2018).

Lactobacillus is known to be the main genus in lactic acid fermentation (Feng et al., 2018), which converts glucose (or alternatives) to lactic acid. This includes bacteria such as *Lactobacillus acidophilus*, *Lactobacillus casei* (Zhou et al., 2018) through the Phosphoketolase pathway (Mao et al., 2015). Lactate dehydrogenase can also be found in *Carnobacterium*, *Enterococcus*, *Lactobacillus*, *Lactococcus*, *Leuconostoc*, *Pediococcus*, *Streptococcus*, *Tetragenococcus*, *Vagococcus* and *Weissella* (Koutinas et al., 2014). Lactate fermentation proceeds as homolactic (one mole of glucose is converted to two moles of lactate) or heterolactic fermentation (one mole of glucose is concerted to one mole of lactic acid with CO_2 and ethanol) (Zhou et al., 2018). Heterolactic fermentation employs additional bacteria including *Bifidobacterium* through the bifidus pathway (Feng et al., 2018). Lactic acid has also been produced during acidogenic fermentation with inoculation of axenic cultures giving a high yield of optically pure product (Waqas et al., 2018). Higher temperatures have also demonstrated improved lactic acid production (Waqas et al., 2018).

In addition to lactic acid, 3-hydroxypropionic acid is a compound of interest due to its use in the synthesis of biodegradable polymers. At present this is only been reported as a significant metabolite of genetically engineered strains of *Escherichia coli* and *Klebsiella pneumonia* (Scheper, 2016).

3.4.5. Dicarboxylic Acids

Dicarboxylic acids have potential as industrially relevant compounds with itaconic acid already produced in industrial-scale fermentation by filamentous fungi (Scheper, 2016) although its production is reported by *Aspergillus terreus* (Koutinas et al., 2014). As a precursor to solvents and polymers, it's estimated global market was between 10,000 and 15,000 tonnes with a price 10 times that of citric acid in 2006 (Levinson et al., 2006).

Listed as a top platform chemical by the US Department of Energy (Werpy et al., 2004), succinic acid has a wide range of applications including as a precursor to 1,4-butanediol, tetrahydrofuran and as a monomer for some biodegradable polymers (Kumar and Longhurst, 2018). Microbial production of succinic acid has been demonstrated from bakery and fruit and vegetable waste by *Actinobacillus succinogenes* and *Yarrowia lipolytica* respectively (Leung et al., 2012; C. Li et al., 2018; Zhang et al., 2013) but the most widely used strains include *Anaerobiospirillum succiniciproducens*, *Actinobacillus succinogenes*, *Mannheimia succiniciproducens*, *Basfia succiniciproducens* and mutations of *Escherichia coli* (Koutinas et al., 2014; Scheper, 2016). One patent reports production of succinic acid from organic waste or biogas or methane by recombinant methanotrophic bacteria, using a group of microorganisms belonging to the following species: *Methylococcus*, *Methylobacterium*, *Methylomicrobium*, *Methylocapsa*, *Methylocella*, *Methylosinus*, *Methylobacillus*, *Methylibium*, *Methylacidiphilum*, *Methylophilus*, *Methylomonas*, *Methylobacter*,

Methylovorus, *Methylocystis*, *Methylovulum*, *Clonothrix* and *Methylococcaceae* (Subbian and Birendra, 2015).

Malic acid has an estimated production of 200,000 tonnes per year with applications as an acidulant and also in cosmetics, pharmaceuticals, paints and plastics (Koutinas et al., 2014). Production is considered to occur via one of three pathways: reductive (pyruvate undergoes carboxylation to oxaloacetate which is then reduced to malate), the glyoxylate pathway (isocitrate is enzymatically converted to succinic acid and glyoxylate which is combined with a water molecule to form malate), and the oxidative pathway through the tricarboxylic acid cycle (West, 2017). Optically pure L-malic acid can be produced via fermentation by *Aspergillus*, *Saccharomyces cerevisiae*, *Zygosaccharomyces rouxii* and genetically engineered *Escherichia coli* strains (Koutinas et al., 2014). Production from coproducts of ethanol and biodiesel has been demonstrated by *Aspergillus* and *Ustilago trichophora* respectively as well as from cellulose and treated lignocellulose by *Thermobifida fusca* (West, 2017).

Other dicarboxylic acids of interest include fumaric acid and adipic acid however their production has only been documented aerobically or synthetically at present.

3.4.6. Furans

Classified as containing an aromatic ring containing four carbon atoms and one oxygen, furans are known to form during thermal decomposition of lignocellulosic material (Whitmore, 1937a). Therefore, they are frequently formed during substrate chemical or thermal pretreatment (Khan et al., 2018) from multiple-step dehydration reactions of furanoses (Y. Wang et al., 2018). Many furans are reported as having an inhibitory effect on the AD process (Anburajan et al., 2017; Khan et al., 2018; Muñoz-Páez et al., 2019).

Hydrothermal pretreatment in particular is known to break down hexoses and pentoses to produce furfural derivatives (Arshadi et al., 2016; Ravindran and Jaiswal, 2016b). One study reported that the presence of hydroxymethylfurfural caused a reduction in yield and changed the dominant bacteria from *Clostridium* to *Lactobacillus* (Anburajan et al., 2017). Furanic compounds are not commonly found in biological systems and few enzymes involved in their formation have been reported (Deng et al., 2018). The secondary metabolite, methylenomycin furan is one of the few examples, reported to induce antibiotic production in *Streptomyces coelicolor* (Sidda and Corre, 2012), as well as 4-(hydroxymethyl)-2-furan–carboxaldehyde-phosphate synthase (MfnB) from methanogen *Methanocaldococcus jannaschii* which can catalyse reactions converting glyceraldehyde-3-P to 4-hydroxymethyl)-2-furan-carboxaldehyde-P (Wang et al., 2015).

Dehydration of C_5 and C_6 sugars has been applied to produce biomass-derived furfural and hydroxymethylfurfural. Derivatives of hydroxymethylfurfural are used to produce biopolymers, fumaric acid, furoic acid furan dicarboxylic acid and furfuryl alcohol, with applications in plastics and chemicals industries (Sawatdeenarunat et al., 2016) resulting in high market value, such as 5-hydroxymethylfurfural which is valued between $330,000 and $386,000 per tonne (Bhaumik and Dhepe, 2015). Furfural produced through acid hydrolysis of agricultural-based biomass, has applications as a platform molecule in the chemicals sector (Dashtban et al., 2012) and market value between $2,800 and $3,300 per tonne (Bhaumik and Dhepe, 2015).

3.5. Hydrolysis Products

3.5.1. Sugars

Sugars are common sweeteners (Kwan et al., 2018; Poli et al., 2011) and energy sources (Bhaumik and Dhepe, 2015; Park et al., 2009) and are generally produced during saccharification of carbohydrates. Glucose, for example, is produced by the depolymerisation of cellulose (Park et al., 2009). Studies have reported recovery of simple sugars, primarily glucose and fructose, using enzyme saccharification from commercial food and beverage wastes (Kwan et al., 2018; Park et al., 2009). Some additional examples of sugars produced during saccharification include xylose, found in xylan, arabinose, found in arabinoxylans (Gupta et al., 2013), galactose, found in milk products, mannose, produced during the depolymerisation of hemicellulose (Hu et al., 2016) and xylulose, formed as isomerisation of xylose during hydrolysis (Bhaumik and Dhepe, 2015).

AD of carbohydrate-rich biomass, followed by downstream enzymatic saccharification of unutilised fractions (cellulose, hemicellulose and lignin) have been considered for converting carbohydrates to sugars (Mathews et al., 2015; Sawatdeenarunat et al., 2016). Recovery of sugar-rich effluents from anaerobic fermentation of food waste has been discussed in the literature and extraction of these reducing sugars could present an opportunity for valorisation (Dahiya et al., 2018). Sugars released in enzyme hydrolysis are ideal substrates for producing alcohols, organic acids and a wide range of biochemicals and biobased products (Sawatdeenarunat et al., 2016) with applications spanning sectors including food, beverage and pharmaceutical industries, as a source of dietary fibre and as a starting material in drug synthesis (Hu et al., 2016). However, a major challenge in the production of sugars is their separation from other sugars (Werpy et al., 2004).

Production and extraction of fermentable sugars is desirable as it can be used as a feedstock for fermentation into other high-value products. The market value of sugars ranges from $500-720 per tonne for glucose and fructose to $1,100-2,800 per tonne for xylose (Bhaumik and Dhepe, 2015). Jung Kon Kim et. al. optimise enzymatic saccharification by maximising reducing sugar content and highlighted that the optimum conditions for hydrolysis and fermentation differ such that it may be favourable to split these stages (Kim et al., 2008).

3.5.2. Amino Acids

Formed during the cleavage of peptide bonds in proteins by exoenzymes, proteases or peptidases, amino acids can then be transported into bacterial cells where they are transformed to organic acids (Dalgleish et al., 2007). Alternatively, they can be used to synthesize cell proteinaceous matter if enough energy is present in the form of carbohydrates (Duong et al., 2019). Examples of amino acid intermediates include alanine, arginine, glutamate, glycine and lysine (Dalgleish et al., 2007).

Limited research has been conducted on amino acids in AD although many studies assume hydrolysis to be the rate-limiting step in protein digestion, as opposed to amino acid fermentation (Flotats et al., 2006; Vavilin et al., 2008). In their study, however, Duong et. al. experimentally determined the opposite, with 19 amino acids detected in the first 8 hours of gelatine digestion (Duong et al., 2019).

Amino acids are subsequently degraded by three metabolic pathways: Stickland reaction (for pairs of amino acids), oxidative deamination and reductive deamination of single amino acids (Shen et al., 2017). To produce amino acids it is required to prevent the general fermentation by Stickland reaction as well as deamination, normally performed by

the *Clostridium* species (Park et al., 2014). Degradation of proteins contributes to alkalinity which is essential as a pH buffer in balancing VFA accumulation (Ma et al., 2018), this can, however, contribute to ammonia toxicity (Dalgleish et al., 2007). Careful control of digester composition through engineered *Clostridium* strains would improve process control (Yokota and Ikeda, 2017).

Production of amino acids from renewable feedstocks remains rare, although chemocatalytic methods have been explored (Deng et al., 2018) alongside microbial cultivation processes (D'Este et al., 2018). Current research mainly focuses on the direct use of cellulose or hemicellulose to produce amino acids. Synthesis of glutamate anaerobically by *Corynebacterium glutamicum* was a notable success in the production of amino acids by fermentation, which has since been extended to other amino acids (Yokota and Ikeda, 2017).

3.5.3. Phytochemicals

Defined as chemicals derived or derivable from plants, phytochemicals can be classed into the following major groups: carotenoids, flavonoids, other phenolics/quinonics, alkaloids, sulphur-containing compounds, phytosterols, polymetric carbohydrates, lipids and volatiles and proteases (Gupta et al., 2014). Phytochemicals are important for the protection of plants (Devappa et al., 2015) and exhibit antimicrobial properties, developed to protect the plant with various proposed mechanisms. By this virtue, many of these substances can therefore be inhibitory to the AD process (Wikandari, 2014).

Phytochemicals that exist in plants generally form part of larger structures and are therefore less bioavailable than their free form, fermentation can release chemically bound molecules (Yeo and Ewe, 2014). Additionally, aerobic microorganisms have long been a

source for bioactive compounds, anaerobic sources, however, have been neglected until recently. The limited research into their production of bioactive compounds indicates that anaerobes are capable of producing a wide range of compounds which could promote human health (Scheper, 2016).

It is often reported that fermentation of food substances can increase total phenolic or flavonoid content (Adetuyi and Ibrahim, 2014; Gupta et al., 2013; Hussain et al., 2016; Martinez-Avila et al., 2014) and this is known to have beneficial effects including antihypertensive, antioxidative and antithrombosis (Scheper, 2016), therefore this presents an interesting research area for AD. In particular, lactic acid bacteria (LAB) fermentation is reported to change the profile of bioactive compounds as a result of several mechanisms such as polymer hydrolysis resulting in increased bioavailability and increase in vitamin, mineral and phenolic compounds, therefore, increasing antioxidant capacity (Septembre-Malaterre et al., 2018).

Extraction of high-value chemicals in the phytochemical class before digestion to biogas have been explored, including solvent extraction, extraction with supercritical fluids, ionic liquids and microwave-assisted extraction, however, this is generally completed as a pretreatment (Arshadi et al., 2016). Examples include the recovery of antioxidants from pomegranate marc at a yield of 106 kg per tonne of dry peel (Qu et al., 2009), polyphenols (anthocyanins, flavonols, phenolic acid and resveratrol) from winery derived wastes (Teixeira et al., 2014), carotenoids and antioxidants from seafood waste (Nazzaro et al., 2018). Production of phenyl acids have been associated with AD overload with phenylacetic and phenylpropionic acid found to form in a substrate dependant manner, furthermore, this was observed to be reversible in the case of mesophilic temperature (Wagner et al., 2019).

3.5.3.1. Phenols / Phenolics

Formed of an aromatic ring with a hydroxyl group, many phenols or phenolics are known to be naturally occurring (Whitmore, 1937b) and thus are of interest in the field of AD. Frequently formed during substrate pre-treatment and regarded as toxic or inhibitory to fuel production (Khan et al., 2018), extraction of phenolics could provide an opportunity for the valorisation of food waste in addition to assisting with any downstream methanogenesis. For example, phenolic molecules released by partially degraded lignin (released during hydrothermal pretreatment) which are inhibitory to fermentation processing can be removed to a large extent by washing (Arshadi et al., 2016).

Vanillin, with applications as a flavouring and in the production of biobased polymers is of increasing interest in the biorefinery concept (Fache et al., 2015). With an estimated global demand exceeding 30,000 tonnes per annum in 2009, it is the most significant flavour compound globally (Laufenberg and Schulze, 2009). *Bacillus subtilis* is a reported producer of vanillin from various starting materials (Rana et al., 2013) and has also been used as a pure bacteria for AD (Xu et al., 2018). Production of vanillic acid has also been reported under saline conditions by *Halomonas elongate* (Abdelkafi et al., 2006). Vanillin is reported to be harmful to cell membranes, damaging them, thereby exposing the cell to extracellular toxic compounds (Khan et al., 2018). In their study, Cabrera et al. reported an accumulation of some phenolics, particularly vanillin, at pH 5 during AD of olive mill solid waste (Cabrera et al., 2019). Lignin in particular has potential as a source of vanillin, however inability to break down this component during AD means this has not yet been exploited (Sawatdeenarunat et al., 2016).

Produced by deacylation of chitin, chitosan (a linear β-(1→4)-linked D-glucosamine polysaccharide) has many attractive properties including biodegradability, biocompatibility, low toxicity, mucoadhesion and non-allergenicity making it a good adjuvant (Rahkila et al., 2016). While traditional methods of chitosan production include chemical methods, several biological methods have been reported to alleviate harmful waste products including a two-stage biological process involving *Lactobacillus pentosus*, followed by the use of protease-producing bacterium *Bacillus thuringiensis* (Ploydee and Chaiyanan, 2014) and a three-stage submerged fermentation with *Serratia marcescens*, *Lactobacillus plantarum* and *Rhizopus japonicus* (Zhang et al., 2017).

3.5.3.2. Flavonoids

Flavonoids generally comprise of a benzene and a benzopyran ring (Bakoyiannis et al., 2019). Flavonoids can be classified into six groups: chalcones, flavones, flavonols, flavandiols, anthocyanins and proanthocyanidins or condensed tannins (aurones are considered a seventh found in certain species) (Falcone Ferreyra et al., 2012). Flavonoids exist in plants and have become of increasing interest due to their bioactive properties (Bakoyiannis et al., 2019; Yang et al., 2018).

Quercetin, found in tomatoes, mangoes, onions (Fermoso et al., 2018) and coffee (Bakoyiannis et al., 2019), is a flavonoid and antioxidant used as an ingredient in dietary supplements and in the food and beverage industry. Quercetin appears to have antidiabetic (Nikfar et al., 2019), cardiovascular (Singh et al., 2018) and anticancer (Baksi et al., 2018) properties. Choi et al. indicated quercetin extraction from onion waste could be increased significantly by enzyme saccharification using cellulose, pectinase and xylase (Choi et al., 2015). In one study, the composition of quercetin was shown to increase after AD of olive

mill waste and piggery effluent (Eusébio et al., 2015) although Wikandari et al. found that spiking systems with quercetin reduced methane production (Wikandari et al., 2014a). *Aspergillus flavus*, *Penicillium rugulosum*, *Thermoactinomyces vulgaris* and *Paenibacillus glucanolyticus* are reported producers of quercetin from rutin (Lu et al., 2012) and flavonoids have also been synthesized from glucose through fermentation by metabolically engineered yeast, with quercetin and kaempferol being in relatively high abundance (Rodriguez et al., 2017).

Baicalin (5,6-dihydroxy-flavone-7-O-glucuronide) is known to perform biological activities such as anti-inflammatory, antitumour, antioxidant and antiviral activities (Yeon Kwon et al., 2017). As such it has applications in traditional Chinese medicine (Ohtsuki et al., 2009). Increased levels of baicalin have been observed following fermentation with *Lactobacillus* (Hussain et al., 2016).

3.5.3.3. Carotenoids

Broadly containing carotenes (α-, β-), xanthophylls (lycopene, lutein and zeaxanthin) and homologs (crocin) (Gupta et al., 2014), carotenoids have industrial relevance as food additives. Carotenoids can be formed from lipids and stored in fatty tissues and give characteristics colours to many plants (autumn leaves, carrots etc.). Microbial production of carotenoids is already of interest as chemical synthesis and extraction from natural sources is low yielding. In particular, the production of carotenoids from agricultural crops using yeast shows great promise (Mata-Gómez et al., 2014). With the global market for carotenoids worth almost $1.5 billion in 2017 and estimated to reach $2.0 billion by 2022 (McWilliams, 2018) research into alternative production methods is expected to increase.

Reported to have strong antioxidant, anti-ageing, anti-inflammatory, sun proofing and immune system-boosting functions, astaxanthin (3,3'-dihydroxy-β,β'-carotene-4,4'-dione) market reached $288 million by 2017 and is estimated to reach $427 million by 2022 (McWilliams, 2018), valued at around $2,500 per kg with approximately 95% currently produced synthetically (Lorenz and Cysewski, 2000). It can be extracted from crustacean waste by chemical strategies as well as by microbial fermentation or enzyme extraction (Sindhu et al., 2019). Astaxanthin commercial production by *Phaffia rhodozyma* has been hampered by low productivity and high cost caused by strain instability and the tendency of mutants to produce less astaxanthin (Jiang et al., 2017).

Additional examples include production of β-carotene is reported by fungus, *Blakeslea trispora* and in their study, Garrido-Fernández et al. demonstrate C_{30} carotenoids are also produced by most strains of *Lactobacillus plantarum* (Garrido-Fernández et al., 2010). Similarly, yeasts have been reported to produce carotenoids, *Rhodotorula spp.* for example (Mata-Gómez et al., 2014).

3.5.3.4. Vitamins

Vitamins encompass several different molecule structures, some of which are covered in this review. Some anaerobes are known to produce vitamins which are beneficial to human health. Micro-organisms found in the human gut, including those from the genera *Bacteroides* and *Eubacterium,* are documented for producing vitamin K, and group B vitamins including thiamine, nicotinic acid, biotin, riboflavin, folates, pyridoxine, pantothenic acid and cobalamin (Scheper, 2016). Presence of certain redox mediators, such as riboflavin, has been shown to affect the redox reaction of amino acids, resulting in high levels of

ammonia as well as increasing the abundance of bacteria related to protein/amino acid degradation as well as VFA fermentation (Huang et al., 2019).

3.5.4. Terpenes

Terpenes have been reported, both as soluble organic matter during AD (Kunacheva et al., 2020) and as volatile organic compounds in biogas (Papurello et al., 2016a; Rasi et al., 2011). Limited research has been conducted surrounding these compounds, the focus is on their presence as an inhibitor, and generally occurs when using citrus waste as a feedstock, where input terpenes levels are high (Forgács et al., 2012; Wikandari, 2014). Several terpenes have a significant market value, although they are rarely of interest in AD as they can inhibit methane production (Wikandari et al., 2013) and contaminate gas (Papurello et al., 2016b; Smet et al., 1999).

Terpenes have a documented presence in biogas produced in landfill (Rasi et al., 2011). One study found levels of volatile organic compounds, specifically terpenes and oxygenated compounds were above safe levels. The study identified three terpenes α-pinene, β-pinene and limonene, although limonene accounted for over 96% of the total amount (Zheng et al., 2020). Another study documented high levels of terpenes in biogas (specifically p-cymene) after anaerobic fermentation in anaerobic/aerobic compositing process (solid-state fermentation followed by dewatering and compositing) (Smet et al., 1999). In contrast, Kunacheva et. al. noted that higher levels were present following methanogenesis as opposed to fermentation, in their study of terpenes and terpenoids as soluble metabolic products after digestion of a synthetic feed comprised of glucose, peptone, meat extract and essential nutrients (Kunacheva et al., 2020). Papurello et. al. monitored trace compound using protein transfer reaction mass spectrometry (PTR-MS) and

noted that isoprene and monoterpenes concentration in biogas increased during AD (Papurello et al., 2016b).

Terpenes are synthesized through the mevalonate (MVA) pathway of archaeal/eukaryotic origin or by the methyl-D-erythritol 4-phosphate (MEP) pathway of prokaryotic bacterial origin (Davies et al., 2015; Steglich, 2007). The skeletal form of terpenes is synthesized through condensation of isopentenyl diphosphate (IDP) and dimethylallyl diphosphate (DMADP). Sequential additions of these units yield geranyl diphosphate (GCP), farnesyl diphosphate (FDP) and geranylgeranyl diphosphate (GGDP), all of which serve as precursors for terpenoids. Further modifications are facilitated by an array of enzymes (e.g. hydroxylases, dehydrogenases, reductases and glycosyl, methyl and acyltransferases) which generate thousands of structures (Lücker et al., 2007). Production of terpenes by algae biomass have been reported in the literature as well as potential pharmaceutical applications of terpenes found in cannabis and hops (Tsolakis et al., 2019).

Limonene (or monoterpene) is a well-known inhibitor of AD (Forgács, 2012; Mizuki et al., 1990; Wikandari et al., 2014b) due to its antimicrobial properties (van Vuuren and Vilijoen, 2007). Its high market value ($9-10 per kg) (Jongedijk et al., 2016) makes it of interest as a commercial commodity chemical. Limonene is found commonly in orange and lemon by-products and has several medicinal properties (Fermoso et al., 2018) and applications within the food and beverage industry (Negro et al., 2016). It is reported that no biosynthetic mechanism has been established for limonene synthesis, despite its detection in the headspace of microbes (Jongedijk et al., 2016). That said, engineered bacteria and yeast have been used to produce limonene through the transformation of limonene synthases. In addition to dedicated production, recovery of limonene from

fermentation systems has also been explored, through capturing methods such as extraction (solvent, supercritical fluid, steam distillation) (Negro et al., 2016), adsorbents, headspace trapping, and gas stripping all evaluated at lab scale (Jongedijk et al., 2016).

Examples of biologically synthesized terpenes include farnesene, produced from yeast using glucose from the sugar can industry (Tsolakis et al., 2019), α-pinene in genetically modified Escherichia coli (Yang et al., 2013), bisabolene in genetically engineered platforms (Peralta-Yahya et al., 2011) and sabinene in a laboratory environment (Zhang et al., 2014). Additionally, Davies et al. (2015) reviewed heterotrophic and photoautotrophic microbial platforms to produce terpenes in large scales, further arguing that marine photosynthetic microbes hold potential for industrial-scale production as they grow in saltwater without requiring exogenous carbohydrate feedstocks (Davies et al., 2015).

4. Challenges and Opportunities

Several AD intermediates have been discussed but exploiting these for valorisation or optimisation faces certain challenges. In addition to the established products (biogas and biofuels), VFAs are already emerging as a potential valorisation opportunity, due to their relative value and ease of extraction, and other intermediates are the focus of research due to their inhibition potential (such as limonene and vanillin), although studies rarely look beyond this. This is, in part, due to the challenges associated with AD, such as complex biology, varying feedstock, inhibition potential and analytical challenges.

The primary challenge faced in expanding the AD map is the complexity of the biological processes occurring within the digesters. This complexity arises from the mixed microbial communities within the reactors and limits the possibility of mapping all the metabolic pathways occurring within the reactor. One limitation of some of the studies cited in this review is that the research is conducted on single strains and, while this adds value in terms of understanding possible mechanisms, additional knowledge is required to understand how interactions and competing pathways impact the overall process. Overcoming this challenge requires extensive characterisation of the microbial communities in collaboration with increased intermediate monitoring.

Variation in feedstock composition also presents significant challenges. Food waste composition is impacted by source (domestic, commercial, agricultural), global location and displays seasonal variability. Improved characterisation of feedstocks, therefore, offers an opportunity to improve understanding. Systematic investigation is required to track specific input compositions through the digestion thereby providing information on the metabolic route and formation of different intermediates. Research would benefit from extending characterisation of substrates, considering not only general compound function, but also specific structure or bond characterisation.

Another challenge in further expanding the AD process map is the potential risk of inhibition. Many of the intermediates highlighted possess antimicrobial properties or create an environment detrimental to the microbial community; therefore, careful management of the microbial balance or innovative product extraction techniques may need to be considered. Similarly, understanding the stress conditions which contribute to the production of intermediates could improve control of the digesters. Alternatively,

monitoring concentration of intermediates could be used as an indicator of system stress. To achieve this, analytical techniques capable of monitoring such molecules down to low concentrations must be identified and selected appropriately.

Even if the biological barriers were to be overcome, any intermediates generated would be low yielding and difficult to analyse or extract. Analysis of intermediates in AD is currently limited, with VFA, pH, alkalinity, and gas composition analysis being the main techniques (Esteves et al., 2013). Analysis of low-level intermediates would require the development of complex methods, deployment of sophisticated technologies (such as IR or RAMAN) or development of novel sensors. Extraction or separation techniques to isolate intermediates are challenging in such heterogeneous mixtures and, although feasible on a lab-scale, in an industrial setting this could potentially add to the economic burden of the process. One example where extraction techniques are facilitating the production of novel intermediates is that of short-chain carboxylic acids which are converted via chain elongation, thus producing MCCAs, possessing lower water solubility allowing them to be removed from the mixture (Yu et al., 2019).

Many of the intermediates discussed could offer an opportunity to expand the AD map. Presence of terpenes, for instance, is not understood metabolically, although they are often reported to be inhibitory, and, as their presence has been detected in the gas phase, the challenges faced in detection and analysis could be simplified. Another potential area of interest is monitoring of amino acids. Existing studies are contradictory in their findings and the broad range of amino acids present in food waste could potentially contribute this. As an important source of nitrogen, more research is required to determine if and how their structure impacts AD. Expanding research into phenolics could also be beneficial. Despite

their presence in fruit and vegetable food waste, only limited research exists addressing their impact on AD. Spiking common phenolics into known substrates would enhance this knowledge and analytical methodologies for their detection are already established (APHA, 1999).

Finally, there are also lessons to be learned from alternative areas of research. Biological fields such as rumen or gastrointestinal biology may provide insight on how many molecules are formed or extracted. Expanding the field of research and working with experts in these fields could expedite progress in the field.

5. Conclusion

Currently, AD is underexploited in terms of food waste valorisation. Although research is ongoing in optimising for production of biogas and biofuels, little has been explored in terms of other intermediates and potential products, the only notable exceptions being VFAs. Additional known intermediates include terpenes, furans and phytochemicals, many of which have high economic value. A greater understanding of the mechanisms which generate these would increase understanding of the AD process and could offer insight for developing a broader control strategy to exploit these intermediates. Whilst this faces significant challenges, this approach could benefit the overall development and implementation of the technology.

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Figure 1: Standard model of AD [adapted from Batstone and Angelidaki, 2014]

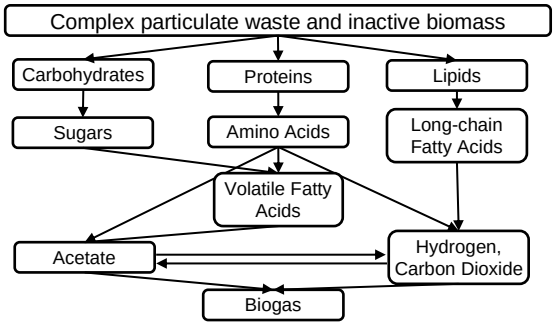

Figure 2: Process map of intermediates during AD

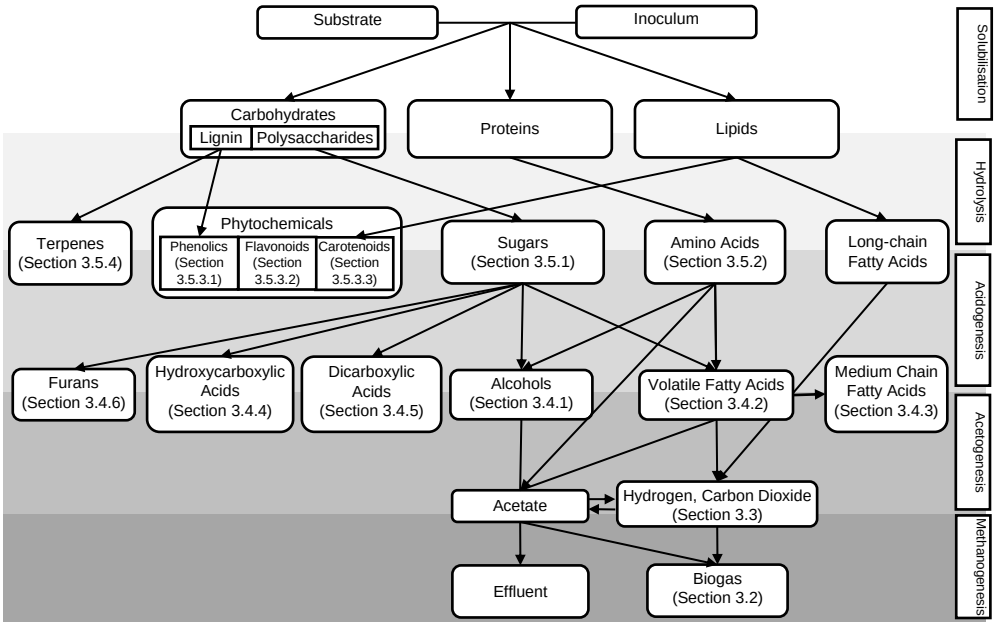

Figure 3: Bibliometric trends for intermediates of AD (2000-2019)

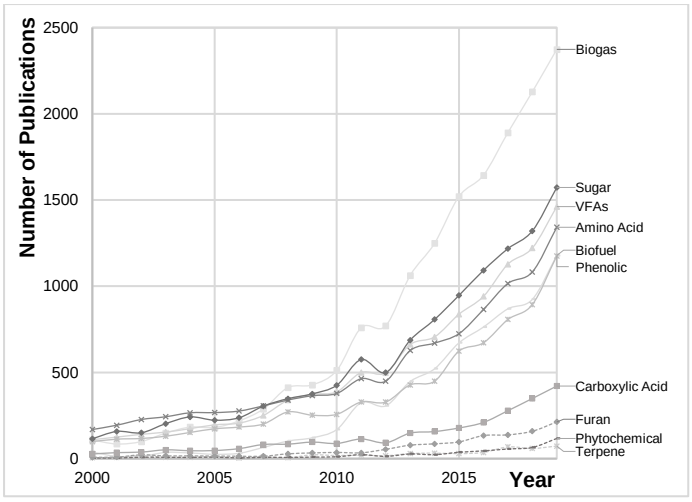

Figure 4: Metabolic pathways of acidinogenic fermentation [adapted from Zhou et. al, 2018]

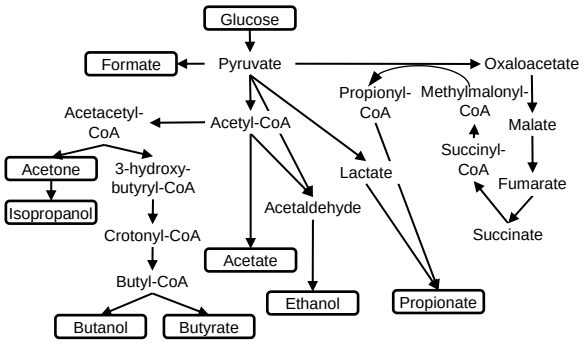

Table 1: Potential intermediates in AD of food waste

Product	Examples	Reference
Biogas	Methane, Hydrogen	(Carmona-Cabello et al., 2018; RedCorn et al., 2018; Sindhu et al., 2019)
Biofuels	Ethanol, butanol, biodiesel, fatty acid methyl ester, dimethyl ester, hydrogen, bio-oil	(Carmona-Cabello et al., 2018; Diaz et al., 2018; RedCorn et al., 2018; Sawatdeenarunat et al., 2016; Sindhu et al., 2019)
Volatile Fatty Acids (VFAs)	Propionic acid, butyric acid, acetic acid and valeric acid	(Carmona-Cabello et al., 2018; Diaz et al., 2018; Esteban and Ladero, 2018; Sawatdeenarunat et al., 2016; Sindhu et al., 2019)
Carboxylic Acids	Hexanoic acid, n-caproic acid	(De Groof et al., 2019)
Hydroxycarboxylic Acids	Lactic acid, hydroxypropionic acid	(Carmona-Cabello et al., 2018; Diaz et al., 2018; Esteban and Ladero, 2018; RedCorn et al., 2018; Sawatdeenarunat et al., 2016; Sindhu et al., 2019)
Di/tricarboxylic Acids	Fumaric acid, citric acid, succinic acid, oxalic acid and malic acids	(Carmona-Cabello et al., 2018; Diaz et al., 2018; Esteban and Ladero, 2018; Nazzaro et al., 2018; Sawatdeenarunat et al., 2016; Sindhu et al., 2019)
Hydroxycinnamic acid	Feruic acid	(Nazzaro et al., 2018)
Sugars	Glucose, D-tagatose, D-mannose	(Sindhu et al., 2019)
Amino Acids	Alanine, arginine, glutamate, glycine and lysine	(Dalgleish et al., 2007)
Phytochemicals/ Biomolecules/ Nutraceuticals	Minerals, vitamins/antioxidants (phenolics & flavonoids) such as astaxanthin, lycopene	(Nazzaro et al., 2018; Sawatdeenarunat et al., 2016; Sindhu et al., 2019)
Flavonoids	Epicatechin, Quercetin	(Nazzaro et al., 2018; RedCorn et al., 2018; Sindhu et al., 2019)
Phenols / Phenolics	Chitin, chitosan, sterols, tocols, syringic acid gentistic, caffeic, p-coumaric, ferulic and sinapic acid, vanillin	(Carmona-Cabello et al., 2018; Nazzaro et al., 2018; RedCorn et al., 2018; Sawatdeenarunat et al., 2016)
Carotenoids	Astaxanthin, colour pigments (e.g. L-tryptophan)	(Nazzaro et al., 2018; Sindhu et al., 2019)
Furans	Furfural and hydroxymethylfurfural (HMF) levulinic acid	(Esteban and Ladero, 2018; Sawatdeenarunat et al., 2016)
Terpenes	Limonene, farnsene, α-pinene, bisabolene, sabinene	(Davies et al., 2015; Peralta-Yahya et al., 2011; Tsolakis et al., 2019; Yang et al., 2013; Zhang et al., 2014)

Table 2: Market value and demand of VFAs

VFA	Approx. Market Value	Annual Global Demand	Applications	Reference
Mixed Acid	2700 $/tonne	No data	Precursor for polyhydroxyalkanoates, reduced chemicals and biofuels	(European Commission, 2018; Woo and Kim, 2019;)
Acetic	400-800 $/ tonne	9-17 million tonnes	Poly adhesives, dyes, food additives, solvent, vinegar, ester production, chemical products.	(Atasoy et al., 2018; Calt, 2015; Scheper, 2016; Zhou et al., 2018)
Propionic	1800-2500 $/tonne	350-470 kilo tonnes	Food preservatives and flavourings, bactericides, pharmaceuticals, plastics, emulsifying agents, aroma additive and animal feed supplement.	(Atasoy et al., 2018; Calt, 2015; Dalgleish et al., 2007; H. Yang et al., 2018; Sindhu et al., 2019)
Butyric	1500 - 2200 $/tonne	70-105 kilo tonnes	Food additives, pharmaceuticals, chemical intermediates, solvents and flavouring agent.	(Atasoy et al., 2018; Calt, 2015; Jiang et al., 2018; Scheper, 2016; Zhou et al., 2018)
Isobutyric	3200 $/ton	No data	Precursor for chemical products	(Calt, 2015; Wainaina et al., 2019)