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Authors

Sekoai, PT
Ghimire, A
Ezeokoli, OT
et al.

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Valorization of volatile fatty acids from the dark fermentation waste Streams-A promising pathway for a biorefinery concept

Patrick T. Sekoai^{a,*}, Anish Ghimire^b, Obinna T. Ezeokoli^c, Subramanya Rao^a, Wing Y. Ngan^a, Olivier Habimana^a, Yuan Yao^a, Pu Yang^a, Aster Hei Yiu Fung^a, Kelvin O. Yoro^d, Michael O. Daramola^e, Chun-Hsiung Hung^f

^a The School of Biological Sciences, The University of Hong Kong, Pokfulam, Hong Kong Special Administrative Region

^b Department of Environmental Science and Engineering, Kathmandu University, Nepal

^c Department of Microbial, Biochemical and Food Biotechnology, University of the Free State, Bloemfontein, 9301, South Africa

^d Energy Technologies Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, 94720, United States

^e Department of Chemical Engineering, Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Hatfield, 0028, South Africa

^f Environmental Biotechnology Lab, Department of Environmental Engineering, National Chung Hsing University, Taiwan

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ABSTRACT

In recent years, much attention has been directed towards the integration of dark fermentation process into a biorefinery concept to enhance the energetic gains, thereby improving the competitiveness of this process. The volatile fatty acids (VFAs) from dark fermentative H₂-producing processes serve as precursors for the microbial synthesis of a broad spectrum of biotechnologically-important products such as biofuels and biocommodities. These products are desirable substrates for secondary bioprocesses due to their biodegradable nature and affordability. This short review discusses the use of acidogenic-derived VFAs in the production of value-added compounds such as polyhydroxyalkanoates (PHAs) alongside the microbial-based fuels (hydrogen, biogas, and electricity), and other valuable compounds (succinic acid, citric acid, and butanol). The review also highlights the strategies that have been used to enhance the extraction of VFAs from acidogenic effluents and other related waste streams. The application of novel enhancement techniques such as nanoparticles during VFAs recovery is also discussed in this work. Furthermore, the work highlights some of the recent advances in dark fermentation-based biorefinery, particularly the development of pilot-scale processes. Finally, the review provides some suggestions on the advancement of dark fermentation-based biorefineries using VFAs that are derived from acidogenic processes.

1. Introduction

The rapid industrialization, coupled with the population growth, has led to massive biomass generation. A recent report from the World Bank has shown that more than two billion tons of biomass residues (agricultural residues, organic fraction of solid municipal waste, food-processing waste, etc) are generated each year globally, and this value is expected to increase to 3.4 billion by 2050, indicating a 70% increase [1,2]. These residues are regarded as suitable feedstocks for the production of alternative fuels because they are highly accessible, reduce the operational costs, and are rich in nutritional composition, i.e. 80–95% volatile solids, and 75–85% moisture [3].

Biomass valorization targeting sustainable energy development is

one of the main focus areas of the 21st century and is being accelerated throughout the world to combat the pressing issues such as environmental pollution, energy crisis, and depletion of fossil fuels [4]. Consequently, biomass residues are valorized into renewable fuels and platform chemicals using various existing technologies [5,6]. Amongst these methods, biological approaches are highly favoured due to their environmental-friendliness and cost-competitiveness [7]. Dark fermentation is seen as the most affordable and carbon-neutral process due to its excellent properties such as the ability to utilize many different wastes, the ability to use inoculum sources from diverse habitats, and the ability to produce hydrogen under ambient temperature and pressure [8,9].

Despite being envisaged as the “future alternative technology”, dark fermentative H₂ production is still affected by various process

* Corresponding author.

E-mail addresses: ptsekoai@hku.ac.hk, patricksekoai@gmail.com (P.T. Sekoai).

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Nomenclature		VS	volatile solids
		VSS	volatile suspended solids
Abbreviations		Units	
COD	chemical oxygen demand	d	day
DCW	dry cell weight	g	gram
HRT	hydraulic retention time	h	hour
MECs	microbial electrolysis cells	Kg	kilogram
MFCs	microbial fuel cells	L	litre
OFSMW	organic fraction of solid municipal waste	mg	milligram
OLR	organic loading rate	mL	millilitre
PHAs	polyhydroxyalkanoates	mol	mol amount
TVS	total volatile solids	t	time
VFAs	volatile fatty acids		

constraints that hinder its commercialization [10,11]. Firstly, the experimental yields are very low, i.e. the microbial yields are around 50% of the theoretical yields due to the accumulation of H₂-scavenging reactions which consume the desired H₂ [12]. Secondly, the organic feedstocks must undergo vigorous pretreatment stages before the acidogenic process (the main dark fermentative H₂-producing pathway), which elevates the process costs [13]. Furthermore, most studies are still conducted under laboratory-scale conditions, implying that the process dynamics for large-scale dark fermentative H₂-producing process are not well understood [14,15].

In recent years, studies have been examining the valorization of dark fermentation effluents into various value-added compounds to enhance the energetic gains and economic value of this bioprocess. At the end of the acidogenic process, the effluents, which mainly consist of volatile fatty acids, alcohols, and other residues, are used as precursors for secondary bioprocesses [2,16]. Volatile fatty acids (VFAs) are reported as being the most critical precursors in biorefinery owing to their functional groups which allows them to be used in various industrial applications including chemicals [17], bioplastics [18], biofuels [16], and wastewater treatment [19]. The demand for VFAs is expected to increase rapidly over the next years due to their numerous applications [19]. For example, more than 7 million tons of acetic acid is produced globally, and this value is expected to reach 15 million tons in 2020 [20,21]. Similarly, the demand for butyric acid is also growing due to its application in animal feed, food, and pharmaceutical industries [22,23]. The global production for butyric acid is estimated at 300 000 tons and has an annual growth rate of 2.5% [24]. Other VFAs such as lactic acid and propionic acid have numerous applications as well [25,26]. The worldwide demand for lactic acid and propionic acid is presently estimated at 150 000 and 400 000 tons, respectively [27]. Currently, the industrial production of VFAs is mainly conducted using chemical processes like the oxidation or carboxylation of precursors such as aldehyde and alkenes [28]. However, the continual use of energy-intensive processes contributes to CO₂ emissions and ecological imbalances [29]. For this reason, there is a paradigm shift in the production of these valuable compounds. Research is now tailored towards the use of acidogenic-derived VFAs to make this technology economically-feasible and environmentally-benign.

1.1. Significance of study and contribution to knowledge

VFAs remain a major untapped resource in dark fermentation effluents due to the process barriers facing this technology, and these are mainly centred around the incomplete conversion of organic feedstocks, as mentioned earlier. This implies that these valuable compounds have not been exploited to their full potential in this research field. From this standpoint, the incorporation of acidogenic-derived VFAs in a biorefinery concept presents a wide range of opportunities for the synthesis of diverse bioproducts. To date, several reviews [10,30–33] have

proposed the integration of biorefinery concept in dark fermentation; however, only a few of these have managed to conduct in-depth literature survey on biotechnological compounds that have been synthesized solely on acidogenic-derived VFAs, particularly the production of PHAs. Furthermore, strategies which optimize the extraction of VFAs during acidogenic fermentations are not well documented in these reports. Therefore, this paper provides a comprehensive overview of the use of acidogenic-derived VFAs as precursors in other bioprocesses. The synthesis of PHAs, biofuels, and other valuable compounds using these VFAs is critically reviewed in this paper. Strategies that have been developed to enhance the extraction of VFAs from the acidogenic processes and other related wastes are also comprehensively discussed. Furthermore, a short section that elucidates the use of novel extraction methods such as nanoparticles in efforts to enhance the recovery of VFAs in these bioprocesses is included. The review concludes with some suggestions that could be pivotal to the advancement of this technology in the future.

2. Application of acidogenic-derived volatile fatty acids

2.1. Polyhydroxyalkanoates

The environmental concerns associated with the continual use of petroleum-based plastics has led to a search for environmentally-friendly alternatives such as polyhydroxyalkanoates (PHAs) [34,35]. PHAs are naturally derived biopolymeric compounds which are produced by a diverse group of microorganisms [36]. They are also known as bioplastics because they have similar physico-chemical properties to conventional plastics [37]. Besides the environmental concerns associated with the use of petroleum-based plastics, the production of bioplastics using renewable feedstocks has been advantageous as these carbon sources reduce the operational costs by 30–40% [38–40].

As highlighted above, these biopolymers can be synthesized by a vast array of microorganisms, i.e. more than 90 bacterial genera have been identified as PHA-producers [6,41] including pure and mixed cultures (see Table 1). From an economic standpoint, the use of pure cultures is not ideal because it escalates the operating costs due to stringent process conditions, the requirements for sterile conditions, and the utilization of monomeric sugars such as glucose and sucrose [38,42]. In recent years, much research has been directed towards using mixed cultures to advance the production of bioplastics using renewable feedstocks such as acidogenic-derived VFAs and waste activated sludge [43]. The production of PHAs using mixed cultures involves these essential steps (i) the extraction/beneficiation of VFAs from the dark fermentation effluents, (ii) enrichment of PHA-storing microbial biofilms, (iii) accumulation of biomass yielding PHAs, and (iv) the recovery of these biopolymers [44,45].

Although studies which involve the valorization of dark fermentation effluents to PHAs are still scarce in the literature, several

Table 1
Production of PHAs from VFAs-containing waste streams.

Feedstocks type	Inoculum source	Reactor type	pH	Temp (°C)	HRT (h)	PHA yield	Reference
Food waste	Acidogenic mixed bacteria	Batch	8	30	24	23.7% DCW	Amulya et al. [38]
Food waste	Industrial wastewater	Fed-batch	7	29	72	36.9% DCW	Reddy and Mohan [46]
Acidogenic effluent	<i>Pseudomonas otitidis</i>	Batch	7	28	48	58% DCW	Reddy et al. [55]
Acidogenic effluent	Mixed anaerobic cultures	Fed-batch	6.0–9.0	29	72	33%	Mohan et al. [56]
Sugarcane molasses	Mixed anaerobic cultures	Batch	7.7	30	4	–	Bengtsson et al. [57]
Municipal wastewater	Activated sludge	Fed-batch	8.5	30	1	34% g PHA/g VSS	Morgan-Sagastume et al. [58]
Acidogenic effluent	Enriched mixed cultures	Batch	7	28	12–48	54 ± 3% DCW	Venkateswar Reddy et al. [47]
Synthetic wastewater	<i>Serratia ureilytica</i>	Batch	7	28	14–48	51 ± 2% DCW	Venkateswar Reddy et al. [47]
Fermented molasses	Mixed cultures	Batch	8.2–8.4	23–25	12	15–39%	Albuquerque et al. [48]
Waste cooking oil	<i>Pseudomonas chlororaphis</i> 555	Batch	6.9	30	16–18	0.52 g/g substrate	Ruiz et al. [49]
Growth medium	<i>Pseudomonas putida</i> Bet001	Batch	6.8	30	48	–	Razaif-Mazinah et al. [50]
Growth medium	<i>Delftia tsuruhatensis</i> Bet002	Batch	6.8	30	48	–	Razaif-Mazinah et al. [50]

–: Not available, DCW: Dry cell weight, h: Hour, HRT: Hydraulic retention time, Temp: Temperature, VSS: Volatile suspended solids.

researchers have been able to demonstrate the bioconversion of waste-derived VFAs into bioplastics using mixed cultures. Reddy and Mohan [46] studied the effects of aerobic and anoxic conditions on PHA production from acidogenic effluents and food waste using mixed cultures. Anoxic conditions favoured an optimal PHA production, while aerobic conditions favoured high substrate degradation. Amongst the studied feedstocks, food waste generated an optimum amount of PHA (39.6%) than the acidogenic effluent (35.6%) due to the high availability of VFAs in food waste. Furthermore, the authors observed diverse microbial communities during PHA production, alongside the hydrolytic enzymes such as dehydrogenase, phosphatase, and protease. This research group also conducted a comparative study on PHA production from pure and mixed anaerobic cultures using synthetic wastewater and acidogenic effluents that were collected from an H₂-producing reactor [47]. The use of mixed consortia and synthetic wastewater enhanced the PHA accumulation to 54% dry cell weight (DCW). On the other hand, the pure cultures of *Serratia ureilytica* only produced a minimum PHA yield of 51% DCW [47]. Albuquerque et al. [48] investigated the effects of fermented molasses consisting of VFAs on PHA production using mixed cultures, under different feeding conditions such as pulse-wise feeding and continuous feeding. It was observed that the continuous feeding strategy resulted in high volumetric productivity and helped to broaden the types of polymeric compounds produced during PHA production. Continuous feeding also increased the production of hydroxyvalerate compounds by 8% in comparison to pulse-feeding [48]. Therefore, this work demonstrated that the desired biopolymeric compounds could be produced using fermentation effluents from the acidogenic reactor [48]. In another study, the production of PHAs was evaluated in a three-stage sequential process using food waste as a carbon source [38]. The first stage involved the production of H₂ alongside VFAs using acidogenic cultures. Thereafter, the VFAs were used for PHA production, which consisted of two-stages, namely the enrichment of PHA-storing cultures (stage 2) and PHA production (stage 3). The PHA-storing consortia were enhanced in a sequencing batch reactor which was conducted under varying feeding cycles of 12–24 h [38]. In this scenario, a high polymeric recovery, as well as VFA removal, was recorded at a feeding cycle of 24 h in both stage 2 (16.3% DCW and VFA removal efficiency of 84%) and stage 3 (23.7% DCW and VFA removal of 88%) [38]. Therefore, this work demonstrated a novel method of simultaneously producing bio-fuels alongside PHAs using renewable and readily available feedstocks such as food waste. Other authors reported the production of PHAs using VFAs that are derived from lipid-rich wastes such as waste cooking oils [49], palm oils [50], waste animal fats [51], and olive mill effluents [52] are also expected to play a pivotal role in accelerating the production of PHAs from waste materials.

In summary, the production of PHAs using VFAs derived from waste feedstocks may be both beneficial and economical because this technology generates industrially-relevant biocompounds that have diverse applications while alleviating environmental problems (Table 2). However, the large-scale production of PHAs using these feedstocks is

still hindered by the low recovery yields. Most studies in literature reported a yield ranging from 24 to 35% DCW, which is very low if this process is to be considered for commercialization [38,53,54]. Other challenges include the strict bioprocess conditions and high purification costs [54]. Furthermore, the production of PHAs using renewable feedstocks is conducted under laboratory-scale conditions which implies that many knowledge gaps still exist in this field. To advance this process, various approaches should be adopted in the future. These include finding feedstocks that produce a high concentration of VFAs, optimizing the process conditions for high VFA yields, and conducting PHA studies at large-scale to acquire deeper insights into the process dynamics.

2.2. Biomethane

Biomethane production occurs in the final stage of the anaerobic digestion process. Herein, the fermentative by-products from the acidogenic and acetogenic stages (which comprises mostly of H₂ and VFAs) are converted into CH₄ (50–70%), CO₂ (25–45%) and other traceable compounds such as H₂S, and NH₃ by various archaeal and bacterial species [59–61]. Although single-stage anaerobic digestion is widely studied in the literature [62,63], this process does not optimally produce biomethane due to variations in growth conditions of acidogenic and methanogenic species [6,59,64]. Consequently, studies have proposed the use of two-stage anaerobic digestion processes to cater for the growth requirements of different microbial groups [65–67]. For example, acidogens are fast-growing microorganisms and usually proliferate under acidic pH and short hydraulic retention times (HRTs), whereas methanogens grow under neutral pH and longer HRTs [68,69]. The use of two-stage anaerobic processes has captured the attention of many researchers over the last decade because it allows for high recovery of VFAs by methane-producing microorganisms [70–72]. Furthermore, the acidogenic stage helps in hydrolyzing the organic substrates into VFAs, which are then utilized by the methanogenic species in the later stage of the anaerobic digestion process [70,73]. Besides, the possibility of pretreating the organic substrates without the need to use energy-intensive methods makes the two-stage process cost-effective [74,75].

Biomethane technologies are gaining increasing attention in various countries across the world due to their environmental friendliness and cost-competitiveness. For instance, countries such as the United States, India, Germany, Brazil, China, United Kingdom, and the Netherlands use this technology to treat their organic wastes while generating valuable energy [76]. The biomethane is either converted into electricity or used for heating purposes [77]. Alternatively, it can be used to obtain a high-purity CH₄ (CH₄>94%) through the CO₂-removal methods, desulphurization, and biogas upgrading methods within the reactor [78,79].

Table 2

Operational parameters affecting the extraction of VFAs from the dark fermentation waste streams.

Substrate	Inoculum	Reactor type	pH	Temp. (°C)	HRT (h)	OLR	VFAs produced	Reference
Organic waste	Granular sludge	Batch reactor	7.0	55	–	–	Acetate Butyrate	Weide et al. [239]
Kitchen waste	Digested sludge	Batch reactor	–	37	–	–	Acetate Butyrate	Slezak et al. [240]
Organic waste	Digested sludge	Batch reactor	7.0–8.0	37	–	–	Acetate Butyrate	Grzelak et al. [241]
Sweet sorghum	<i>Clostridium thermosaccharolyticum</i>	Batch reactor	7.0	55	–	–	Acetate Butyrate	Islam et al. [242]
Food waste	Granular sludge	Batch reactor	6.0	30	–	–	Acetate Butyrate Propionate	Yin et al. [69]
Organic waste	Granular sludge	Batch	6.0	35	–	–	Acetate Butyrate	Trevisan et al. [243]
Food waste	Anaerobic sludge	Semi-continuous reactor	5.0–7.0	37	–	–	Acetate Butyrate	Farouk et al. [138]
Kitchen waste	Anaerobic sludge	Semi-continuous reactor	7.0	35	–	–	Acetate Butyrate Formate	Zhang et al. [139]
Mushroom waste	Anaerobic sludge	Batch reactor	8.0	55	–	–	Propionate Acetate Butyrate	Lay et al. [140]
Sucrose	Anaerobic sludge	Batch reactor	8.95	35	–	–	Propionate Valeric acid Butyrate	Choi and Ahn [141]
Synthetic medium	Dewatered sludge	Semi-continuous reactor	6.6–7.1	55	–	–	Propionate Acetate Butyrate	Hao and Wang [148]
Waste activated sludge	–	Batch reactors	8.0–9.0	35, 55	–	–	Propionate Valerate Acetate	Zhang et al. [150]
Wastewater	Activated sludge	Semi-continuous reactor	10–11	19–25	14.9	21 day	Valerate Acetate Butyrate Propionate	Liu et al. [149]
Substrate	Inoculum	Reactor type	pH	Temp. (°C)	HRT (h)	OLR	VFAs produced	Reference
Food waste	Granular sludge	Batch reactor	6.0	35	–	–	Acetate Butyrate	Jia et al. [244]
Glucose	Activated sludge	Batch reactor	5.4	26	–	–	Acetate Butyrate Propionate	Infantes et al. [245]
Organic waste	Compost	CSTR	6.5	37	20–30	10.8 g COD/L.d	Lactate Acetate Butyrate	Khanal et al. [246]
Food waste	Seed culture	CSTR	>4.0	37	12	6 g/L	Propionate Acetate Butyrate	Han et al. [247]
Starch	Anaerobic sludge	CSTR	5.3	35	12	20 g COD/L	Acetate Butyrate	Arooj et al. [248]
Cornstalk	Anaerobic sludge	PBR and UASBR	~7.0	37	12	0–8 g COD/L	Acetate Butyrate Succinate	Si et al. [249]
Food waste	Anaerobic sludge	Batch reactor	7.0	35	–	–	Acetate Butyrate Propionate	Liu et al. [250]
<i>Macrocystis pyrifera</i> biomass	Anaerobic sludge	Batch reactor	7.0	37	–	–	Acetate Butyrate	Zhao et al. [251]
Microalgae	Anaerobic sludge	Batch reactor	7.0	35	–	–	Butyrate	Usmanbaha et al. [252]
Cheese whey	Poultry sludge	CSTR	4.0–4.5	30	6	20 g COD/m ³ . day	Acetate Butyrate Propionate Iso-butyrate	Rosa et al. [253]
Cheese whey	Granular sludge	UASBR	5.3–5.5	35	13–8	20–30 g COD/L. day	Lactate Acetate Butyrate	Carrillo-Reyes et al. [254]
Sugarcane vinasse	Anaerobic sludge	AFBR	4.0–5.0	22	6	5 g COD/L	Propionate Butyrate Propionate	dos Reis et al. [255]
Glycerol waste	<i>Enterobacter aerogenes</i> ATCC 13048	UASBR	5.5	37	–	50 g COD/L. day	Acetate Formate	Reungsang et al. [256]

:- Not available, COD: Chemical oxygen demand, CSTR: Continuous stirred tank reactor, UASBR: Upflow anaerobic sludge blanket reactor, PBR: Packed bed reactor, AFBR: Anaerobic fluidized bed reactor, OLR: Organic loading rate, Temp.: Temperature, VFAs: Volatile fatty acids.

2.3. Electricity

Microbial fuel cells (MFCs) represents an innovative approach of converting the VFAs from the dark fermentative effluents into electricity production using various anaerobic consortia [80,81]. MFCs are bio-electrochemical systems consisting of two compartments, namely the anodic and cathodic chamber [82]. In the anodic chamber, the VFAs are metabolized into electrons and protons through the aid of microorganisms obtained from various microenvironments [83]. These electrons are transported into the cathodic chamber through an external resistor in order to produce electricity, while the protons pass through the permeable material and react with oxygen to form water as illustrated in Fig. 1A. The anodic and cathodic reactions are represented by Eqs. (1) and (2), respectively, with acetate as a carbon source [84,85]. Different types of MFCs have been used for electricity generation, including single-chambered MFC, two-chambered MFC, stacked MFC, and upflow

MFC [86]. Amongst these designs, two-chambered MFCs are widely used in many electricity-generating experiments due to their simple operation and low cost [86].

Studies reported high energetic gains using MFCs as a secondary pretreatment technology. For instance, Sharma and Li [87] observed an optimum power density and coulombic efficiency of 4200 mW/m² and 5.3%, respectively, from the VFAs present in the dark fermentation effluents. The authors also recorded an energy recovery of 559 J/L and chemical oxygen demand (COD) removal efficiency of more than 90% from this study [87]. Mohanakrishna et al. [83] also recorded a maximum power density of 111.76 mW/m² and COD removal of 80% using the VFAs from the acid-rich dark fermentative effluents which were generated in the acidogenic sequential batch biofilm reactor. In addition, the MFC process was able to remove 80% of COD, 79% of VFAs, 78% of carbohydrates, and 65% turbidity [83]. The high COD removal in these studies is mainly due to the high concentrations of

Fig. 1. Acidogenic-derived VFAs used in a microbial fuel cell (A) and microbial electrolysis cell (B). Adapted and modified from Du et al. [84].

acetate, butyrate and propionate in the effluents, which are suitable for electrogenic bacteria in MFCs [88,89].

In a similar study, it was reported that acetate produced a power output (506 mW/m^2) that was 66% higher than that of butyrate (305 mW/m^2), therefore signifying that this substrate is an excellent carbon source for electricity-producing microorganisms [88]. Nevertheless, other factors such as process parameters, substrate types, and inoculum source also contribute towards bioelectricity generation, and therefore these variables need to be optimized during electricity production [90, 91].

In light of the above findings, it is evident that MFCs could play a significant role in the biotransformation of VFAs from the dark fermentative effluents into value-added by-products such as electricity. Despite these promising outcomes, most MFCs processes are still carried out using miniaturized reactor systems such as shake flasks [16,92]. Thus, more pilot-scale studies should be done to acquire in-depth insights into the process dynamics during electricity production. Such in-depth insights could ultimately pave the way for large-scale electricity production using this technology [16,92].

2.4. Hydrogen

During the dark fermentative H_2 production, the substrates are partially converted into H_2 due to the formation of side-reactions which results in the production of VFAs, alcohols, CO_2 , and other metabolites [15,93]. The unutilized metabolites are integrated into two-stage H_2 production processes in order to enhance the energetic gains, as mentioned earlier [94]. The VFAs that are present in these effluents serve as a carbon source in photo-fermentation and microbial electrolysis cells [95]. In the photo-fermentation process, purple non-sulfur bacteria such as *Rhodospirillum rubrum* sp. converts VFAs into H_2 under light-mediated conditions [96]. Purple non-sulfur bacteria are considered as desirable candidates for large-scale H_2 production because they have a high substrate conversion efficiency, they have a high degree of anaerobiosis, they can produce H_2 under different wavelengths (522–860 nm), and utilize a wide variety of precursors or substrates [97]. They also consist of key enzymes such as nitrogenases and hydrogenases, which regulate the H_2 -producing pathways [98].

Operational parameters such as pH, temperature, C/N ratio, and inoculum source play a crucial role in shifting the metabolic pathways towards higher H_2 production from the VFAs [99,100]. However, before the photo-fermentation process, the dark fermentative effluents must undergo pretreatments (dilution and centrifugation) to remove the colloidal particles in the waste streams [94,101]. The photosynthetic bacteria have also been shown to be sensitive towards certain types of VFAs [102,103]. For example, it has been reported that acetate, butyrate, and malate are ideal carbon sources, while substrates like sucrose and glucose are not suitable for these microorganisms [104,105]. Besides the role of VFAs on H_2 production, other growth factors such as micronutrients also play an essential role in the overall process performance. Therefore, the photosynthetic medium is usually supplemented with metal additives (Ni^{2+} , Mg^{2+} , and Fe^{2+}), yeast extract, glutamate, albumin, and molybdenum for enhanced H_2 recovery [96].

Microbial electrolysis cells (MECs) are an alternative option for producing H_2 from the VFAs that originate from the dark fermentative streams. This technology is derived from MFCs but applies direct voltage in the cathodic chamber because the process does not occur spontaneously as shown in Fig. 1B [106,107]. The electrochemically active bacteria (in the anode) converts the VFAs and releases the electrons and protons that are passed into the cathodic chamber via an external circuit and permeable material, respectively [85,108]. Similar to MFCs, these biotechnological systems are beneficial because they use diverse

microbial species and substrates during H_2 production [16]. The production of H_2 with acetate as a substrate is elucidated with Eqs. (3) and (4), respectively [109]. Several studies have successfully used this technology to valorize the dark fermentation effluents. These studies used substrates such as industrial wastewaters [95], cellulose [110], waste activated sludge [111], cheese whey [111], and other organic feedstocks. However, there is still little knowledge on how various factors affects the behaviour of MECs in large-scale applications. Recent efforts have focused on microbial population dynamics to understand the microbial biofilms, which actively participate during the bio-electrochemical production of H_2 [112]. San-Martín et al. [112] recently studied the microbial diversity during H_2 production using a 16-L MEC reactor. There was a little variation in microbial communities during the long-term H_2 production process, with *Firmicutes* and *Bacteroidetes* being the dominant phylum. The authors also reported a stable performance during the course of the process and an optimal H_2 production rate of 15.3 g N/d.m^2 [112]. Furthermore, it was revealed that these bacterial groups contributed to forming complex biofilms in the anode [112]. The changes in the biofilm communities of the anodic chamber were also examined in an acetate fed-batch single-chambered MEC by Sciarria et al. [113]. Diverse microbial communities were identified in the anodic compartment and these microorganisms contributed towards biofilm formation [113]. Hence, these studies underscore the importance of having biofilm-forming microbial communities in MECs in order to enhance the bioelectrochemical H_2 production process. Earlier studies focused on optimizing the process parameters such as pH, temperature, and reactor design (anode, cathode, and electrolyte) [109, 114].

Besides the application of MECs in H_2 production as documented in these studies, these bioelectrochemical reactors have been shown to be useful in the removal of impurities (mainly CO_2) during biogas production and this approach yields high CH_4 content (>90%) [59]. The purified (upgraded) biogas can be used for various purposes such as electricity generation, automotive engines, and in natural gas pipelines [59].

Electrohydrolysis is also used to generate H_2 using VFAs from the dark fermentation effluents. In this approach, voltage is used to generate protons from the electrohydrolysis of VFAs, and the electrons originate from the metal electrode (using Cu electrode as an example) [115]. This process is explained with Eqs. (5) and (6) [115,116]. An exciting feature about this technology is that it allows an *in-situ* H_2 production [117], which implies that this process enables direct utilization of waste-derived VFAs in the reactor. However, studies on H_2 production using electrohydrolysis are scantily reported in the literature. An earlier study by Tuna et al. [115] successfully produced H_2 using VFAs from the dark fermentation effluents of wheat powder. In this work, the authors examined the effects of voltage, pH, and VFA concentration on H_2 production. The optimal conditions for enhanced cumulative H_2 production (110 mL) were reported to be 2.0, 3V, and 5g TVFA/L, for medium pH, applied voltage, and VFA concentration, respectively [115]. Other authors reported a novel approach of treating the dairy sludge using an *in-situ* electrohydrolysis method [118]. A cumulative H_2 production of 1051 L and H_2 content of 72% was achieved at an influent concentration of 7%, input voltage of 2 V, and an HRT of 15 days, which led to a remarkable COD removal efficiency of 74% [118].

2.5. Biodiesel

Biodiesel has attracted enormous attention amongst various stakeholders (e.g., scientists, government, and businesses) over the last decades owing to its numerous benefits such as low CO₂ emissions, high degradable nature, and its ability to use diverse feedstocks [119,120]. Biodiesel consists of long-chains of alkyl esters which are produced during the transesterification process [120,121]. It is widely known that the majority of the world's biodiesel is produced from edible crops such as sunflower oil, soybean oil, rapeseed oil, and coconut oil, amongst other oils [122,123]. Nevertheless, the “food vs fuel” debate has reinvigorated scientists to look for alternative ways of producing biodiesel, particularly the use of non-edible feedstocks [124–127]. Since the dark fermentative effluents cannot be directly used for biodiesel production, it has been suggested that the VFAs from these effluents should firstly be converted into lipids using oleaginous microorganisms and then use the synthesized lipids in the transesterification process [128,129]. Interestingly, the microbial lipids produced from the waste-derived VFAs have been reported to have similar chemical characteristics (fatty acid composition) to other feedstocks such as soybean oil and jatropha oil [130]. However, there are no studies in the published literature regarding the synthesis of lipids using VFAs that are directly derived from the dark fermentation effluents.

2.6. Other applications of VFAs that are derived from the dark fermentative streams

Besides the bioconversion of acidogenic-derived VFAs into the aforementioned products, these fermentative by-products have also been used in other biotechnological methods such as denitrification process [131], removal of toxins in wastewaters [132], and production of alcohols such as ethanol [133] and butanol [134,135]. Nevertheless, there is also a paucity of such studies in the literature, which implies that more work is still needed in the bioconversion of these effluents to other value-added products. Fig. 2 summarizes the integration of dark fermentation with other microbial processes such as H₂ production, biogas, biodiesel, electricity generation, and PHAs.

3. Parameters affecting the recovery of acidogenic-derived volatile fatty acids

3.1. Medium acidity

Medium acidity is evaluated in the form of pH and is regarded as one of the most crucial parameters that affect the production of VFAs during the valorization of organic wastes because it regulates the acidogenic-solventogenic process and hydrolysis rate [92,136]. There are inconsistencies regarding the optimal pH values in literature due to a wide spectrum of feedstocks used in anaerobic studies [137]. However, neutral pH values (5.5–7.0) are considered to be optimal for the production of VFAs [136]. Recently, Farouk et al. [138] reported that a pH range of 5.0–7.0 favoured the production of acetate and butyrate when food waste was used as a substrate. These intermediates accounted for more than 60% of the total VFAs during the biogenic process [138]. Similarly, Zhang et al. [139] observed that pH 7.0 favoured the conversion of kitchen waste (rich in protein content) into VFAs. A plausible explanation for this phenomenon may be because proteins that are stored in this substrate are usually converted into ammonia under acidic pH conditions, thereby elevating the buffering capacity of the medium [139]. Other contradicting results were also reported with regards to the optimal pH. Using mushroom as a carbon source, Lay et al. [140] evaluated the effect of various inoculums such as primary sludge, secondary sludge, cow dung, and pig slurry on VFAs production at pH 8.0. The major VFAs produced during the acidogenic bioprocess were acetate and propionate and accounted for 86.8% and 20.0%, respectively, of the total VFAs when cow dung was used as the inoculum. In another study, Choi and Ahn [141] observed that during the anaerobic conversion of sucrose and piggery waste, butyrate was the main by-product when the pH was maintained at 8.9. High pH values have been shown to enhance the digestibility of feedstocks and the ability to inhibit unwanted microbial communities, which ultimately results in increased VFAs production [142–144]. Overall, these findings essentially show that although the production of VFAs is highly dependent on the operational pH, the type of feedstocks used during the process also affects the composition of these by-products.

Fig. 2. A schematic diagram illustrating the integration of dark fermentation with other biotechnological processes. Reprinted from Ref. [30], with permission from Elsevier.

3.2. Temperature

Temperature is another crucial variable which controls the formation of VFAs, microbial communities, enzymatic activities, and conversion of substrates [145,146]. VFAs are generated under both mesophilic (20–45 °C) and thermophilic (>45 °C) conditions [147,148]. Thermophilic processes are mostly adopted in VFAs production because they possess several benefits such as high digestibility of substrates, inhibition of unwanted microbes, and minimizes the risks of contamination [148,149]. Hao and Wang [148] observed that thermophilic fermentation resulted in VFAs production that was ten times higher than that of mesophilic conditions without the need to adjust the pH of the medium. Zhang et al. [150] reported that thermophilic conditions enhanced the rate of hydrolysis, thus resulting in high VFAs production. In a pilot-scale study, Liu et al. [149] obtained an optimum VFAs yield of 261.32 mg COD/g VSS during the thermophilic conversion of domestic effluents. Acetate was the main metabolite during the three-stage fermentation process, accounting for 32.21%–57.69% of the total VFAs. In addition, Wilson et al. [151] observed that increasing the temperature from 35 to 57.5 °C enhanced the VFAs production due to a shift in microbial communities during the anaerobic process. As a result, there was a significant decline in the archaeal populations during the transition from mesophilic to thermophilic conditions, which implies that the growth of acidogenic species was favoured during the anaerobic process [151]. These results correspond with existing knowledge since acidogenic pathways have been reported to produce high yields of VFAs than solventogenic pathways when using food waste and mixed microbial cultures [68,152].

3.3. Substrate types

It is widely known that the substrates play a pivotal role in VFAs production during anaerobic processes. Hence, complex substrates have been considered in the enrichment of VFAs in recent years. These include food wastes (e.g. kitchen, canteen, fruits, and vegetables), agricultural wastes (e.g. cornstalk, cassava, perennial grass, bean husk, bagasse, wheat straw, and rice straw), and industrial wastes (e.g. cheese whey, brewery waste, and olive mill), as shown in Fig. 3 [68,153]. Before the use of these feedstocks, many VFAs production studies relied on pure sugars such as glucose and sucrose [154,155]. However, from a financial viewpoint, these pure sugar feedstocks are not ideal for the enhancement of VFAs due to the high operational costs that will be incurred [6,116]. Therefore, researchers are now exploiting organic wastes as viable alternatives because of their cost-competitiveness and the advantage that their utilization will help reduce their hazardous effects on the environment [156–158].

Amongst the aforementioned substrates, food wastes are extensively utilized due to their rich nutritional properties. These carbon sources consist of high biodegradable matter (15–20% TVS), high nitrogen (2–15 g/kg), and phosphorous (0.5–1.5 g/kg) contents [6], which promotes the acidogenic pathways, resulting in high VFAs production [6]. Furthermore, food waste comprises of other essential macromolecules such as lipids, proteins, and carbohydrates which also enhance VFA production during the fermentation process [6].

Several studies have shown that these wastes enrich VFAs production. Recently, Cheah et al. [159] reported an increment of 4.1–9.0% in VFAs production when using a combination of canteen food waste and a varied (25–45%) amount of compost (the inoculum) under batch fermentation conditions. The authors also revealed that the addition of 2.5% (w/w) of compost and operating the bioprocess under semi-continuous conditions led to a remarkable VFA increase of more than 50% [159]. Jayakrishnan et al. [160] optimized the production of VFAs using agro-industrial effluents (rice mill effluent and brewery effluent). The total VFAs increased from 1897 to 2437 mg/L when using heat-treated effluents. Furthermore, acetic acid was the main VFA during the bioconversion of the pretreated effluents. The use of these

Fig. 3. Biomass residues used in VFAs production. Adapted and modified from Rehan et al. [176].

effluents was instrumental in this because the process pH was successfully maintained within the acidic range, which in turn favoured the enhancement of VFA production [160]. It has been shown that the degree of acidification is the key factor affecting the production of VFAs [54,161]. The degree of acidification is defined as the initial amount of COD that is converted into VFAs and other metabolites [54,161]. A study by Silva et al. [162] showed that carbohydrate-rich waste streams maximized the degree of acidification during the fermentation process, resulting in high VFA content. In their study, Silva et al. [162] achieved an optimum degree of acidification (~40%) with total VFA production of 2707–3374 mg/L as COD by utilizing cheese whey, sugarcane molasses, and organic fraction of solid municipal waste (OFSMW). In contrast, landfill leachate and soapy slurry waste produced low degrees of acidification of 2 and 6%, respectively. Other waste products such as olive mill, glycerol, and winery effluent also evaluated in the study by Silva et al. [162] yielded a degree of acidification of 11–13% which corresponds to a total VFA content of 934–1460 mg/L as COD [162]. A possible explanation for the high VFA production in cheese whey, sugarcane molasses, and OFSMW may be due to the biodegradable nature of these substrates as substantiated in a similar study [92]. Surprisingly, the sludge, particularly the primary sludge, is usually known for its high VFA content but this is dependent on the type of biomass used as it affects the acidogenic process [162], and that could be the case. Elsewhere, it was shown that the primary sludge could produce high amounts of VFAs (197–256 mg COD/g VSS) than the activated sludge (11.3–256 mg COD/g VSS) but this was also dependent on the nature of the feedstock [163].

Research studies are also shifting towards co-digestion processes as it has been shown that the co-digested substrates offer several merits in anaerobic fermentation which subsequently leads to enhanced VFA production (see Table 3). Such merits include the stabilization of pH, an optimum carbon to nitrogen ratio, and enhanced acidogenic activities [164,165]. Lomborg et al. [166] used co-digested feedstocks of manure

Table 3

Effects of co-digested substrates on the recovery of volatile fatty acids during dark fermentation.

Co-digested feedstocks	Inoculum source	pH	Temp (°C)	HRT (h)	OLR	Effects of co-substrates on VFAs recovery	Reference
Food waste + molasses	Anaerobic mixed sludge	7.2	35	–	–	The feedstocks provided a suitable nutritional content and produced the desired metabolites (acetate, H ₂ , CH ₄ and CO ₂).	Nguyen et al. [257]
Bean husk + OFSMW + cornstalk	Anaerobic mixed sludge	7.9	30.29	86.26	–	Co-digestion enhanced the carbon/nitrogen ratio and also increased the recovery of VFAs (acetate and butyrate) alongside H ₂ . These feedstocks also contributed in maintaining the optimal pH range of 7.0 to 7.0	Sekoai and Kana [258]
Cheese whey + sugarcane bagasse	Anaerobic mixed sludge	7.06	55	6	2 g COD/L	Co-digestion favoured the dark fermentation process and provided synergist nutritional complementation.	Ramos and Silva [259]
Corn stover + FVW	Anaerobic mixed sludge	7	35	–	–	This strategy increased the acidogenic pathway and was also effective against the excessive production of unwanted metabolites.	Rodríguez-Valderrama et al. [260]
Sugarcane bagasse + pineapple peels	Anaerobic mixed sludge	6.5–7.5	35	–	–	The ratio of acetic to butyric acids was >0.79, which implies that the H ₂ -producing pathways were predominant during dark fermentation.	Robledo-Narváez et al. [261]
Potato + Rice + Lettuce + Banyan leaf	Anaerobic mixed sludge	5.5	37	–	–	The acetate- and butyrate-type fermentations were triggered during the dark fermentation process.	Dong et al. [170]
Sugarcane bagasse + water hyacinth	Anaerobic mixed sludge	6.5	37	–	–	The overall substrate conversion efficiency was increased to 86%, and a maximum energy recovery of 8.97 kJ/g COD was achieved.	Kumari and Das [262]
Coffee residues + sugarcane vinasse	Anaerobic mixed sludge	5.0–6.5	55	1320	0.19 kg VS/m ³ .d	Co-digestion was effective in the production of biohythane (H ₂ and CH ₄) and butyrate during thermophilic biogas conditions.	Pinto et al. [263]

HRT: Hydraulic retention time, FVW: Fruits-and-vegetables wastes, OFSMW: Organic fraction of solid municipal waste, OLR: Organic loading rate, Temp: Temperature.

and maize silage as a way of improving the VFAs during the anaerobic digestion process. The VFAs content increased from 1.3 to 22.3 g/L during the course of the fermentation process. In another co-digestion process, Cheah et al. [167] reported a significant increase in VFA production using co-digested substrates of OFSMW and food waste. The VFA content increased from 9.8 to 11.5 g/L in the semi-continuous lab-scale reactors. Contrary to what is known in literature, the authors revealed that alkaline pH (pH 9.0) led to higher VFA production when compared to near-neutral pH (pH 6.0) with acetic acid (>90%) being the main metabolite [167]. Under alkaline conditions, the free ammonium ions were at an optimum concentration, which led to a subsequent increase in COD solubilization (14–16% higher than the acidic conditions) resulting in high acetic acid production [167].

In addition to the influence of substrates on the quantitative production of VFA, the types of feedstocks used in the anaerobic processes also affect VFA production qualitatively. As a consequence, it has been shown that carbohydrate-rich waste streams favour the enhancement of acetate- and butyrate-producing pathways [168]. Carbohydrate-rich substrates are easily converted by microbial enzymes into monomeric sugars which are immediately used up in the acidogenic pathways during VFA production [69,169]. This was substantiated by Dong et al. [170] when investigating various organic wastes such as potato, rice, and lettuce under mesophilic conditions. The primary intermediates were acetic and butyric acid for potato and lettuce, respectively, accounting for more than 70% (w/w) of the total VFAs in each process. This suggests that acetate- and butyrate-type fermentations were triggered in these bioprocesses [170]. Similarly, Taheri et al. [171] observed that during alkaline sludge pretreatment, the acetate- and butyrate-type fermentations were induced during the microbial conversion of glucose into H₂ and VFAs when the substrate concentration was varied from 3.75 to 15 g/L.

In comparison to carbohydrates, lipids and proteins are less suitable for VFA production due to their chemical composition. The hydrolysis of lipids produces long-chain fatty acids which are not easily degraded by acidogenic microorganisms [172]. In addition, the adherence of lipids onto the cell wall of the bacteria inhibits the metabolism of anaerobic microorganism [173]. Proteins are also characterized by a low biodegradability due to their tertiary and quaternary structure, which makes them less susceptible to enzymatic breakdown [174]. As opposed to carbohydrates, the hydrolysis efficiency of proteins is typically in the

range of 40–70%. Therefore, the hydrolysis of proteins is considered a rate-limiting step during acidogenesis [175].

3.4. Inoculum

The production of VFAs is mediated by various groups of microorganisms with diverse nutritional and operational requirements, as demonstrated in Table 1. These include the hydrolytic bacteria, acidogenic bacteria, acetogenic bacteria, and methanogenic archaea [177, 178]. These biocatalysts are further classified into pure (isolated strains) and mixed consortia (obtained from various environmental habitats such as anaerobic sludge, compost, and soil) [179]. However, mixed consortia are more suited for VFAs production owing to their numerous advantages such as their ability to metabolize a wide spectrum of substrates, tolerance of acidic and alkaline pH, simplicity of process steps as no sterility is required, and the reduction in the process costs [180]. Furthermore, these cultures form a synergistic relationship with other microbes during the acidogenic process, which results in the enhancement of VFAs [181,182]. Amongst the microbial species, methanogens are not suitable for VFAs production because they convert these metabolites into methane during the last stage of anaerobic digestion [183, 184]. It has been reported that the VFAs alongside H₂ are metabolized by the hydrogenotrophic and acetoclastic methanogens in methane-producing pathways, which in turn reduces their concentration in the fermentation medium [185,186]. For this reason, various strategies have been adopted over the past years in order to inhibit the proliferation of methanogens during acidogenesis. The most common approaches used in the inhibition of methanogens are the use of inhibitors, acid-, alkaline-, microwave- and biological pretreatments amongst other methods [187]. However, these pretreatment regimes will escalate the process costs especially at large-scale operations. Thus, studies are now using innovative methods such as real-time monitoring tools (e.g., sensors and actuators) in order to maintain the optimal parameters such as pH and temperature during VFA production [188–190]. Some of the dominant microbial phyla (and genera) involved during acidogenesis are summarized with a phylogenetic tree in Fig. 4. A majority of these bacterial species belongs to the Firmicutes phylum, including obligate and facultative anaerobes such as *Clostridium* sp., *Pseudomonas* sp., *Bacteroides* sp., *Bacillus* sp., and *Desulfobacter* sp., amongst others (Fig. 4).

Fig. 4. The 16S rRNA gene-based tree showing the relatedness of acidogenic-producers.

In addition, the variation in the inoculum sources leads to changes in the metabolic pathways that govern the production of VFAs [68]. Typically, the distribution of the major fermentative by-products reflects the main metabolic pathways that are adopted by the microbial consortia during the acidogenic process [191]. The acidogenic fermentation pathways usually comprises of (i) acetate fermentation (Eq. (7)), (ii) butyrate fermentation (Eq. (8)), (iii) propionate fermentation (Eq. (9)), (iv) lactate fermentation (Eq. (10)) and (v) ethanol fermentation (Eq. (11)) [68]. Amongst these pathways, acetate and butyrate pathways are regarded as the most common intermediates during the acidogenic conversion of organic feedstocks alongside with H_2 [192,193]. However, the production of these by-products is also governed by other operational parameters such as pH, temperature, substrate type, organic loading rate, partial pressure, and hydraulic retention time [194].

3.5. Hydraulic retention time and organic loading rate

Hydraulic retention time (HRT) and organic loading rate (OLR) are applied in acidogenic systems as well, particularly in continuous bio-processes [195,196]. Many studies have shown that longer HRTs offer microorganisms sufficient time to metabolize the substrates [197,198]. At the same time, a further increase in HRT can reduce the production of VFAs because of the acidogenic-solventogenic transition stage [6,199]. A study by Lim et al. [200] demonstrated that increasing the HRT from 4 to 8 days enhanced the production of VFAs during the acidogenic fermentation of food waste. In contrast, there was no significant increase in VFA production when the HRT was further increased to 8 and 12 days [68,200]. Similarly, Banerjee et al. [201] observed a significant increase in VFA production after increasing the HRT from 0.75 to 1.25 days in a bench-scale acidogenic process using starch wastewater and municipal sludge as feedstocks. In terms of obtaining the specific acid production,

it has been shown that the microbial communities within the acidogenic reactor can be manipulated by regulating the HRT. For example, Chen et al. [202] found that an HRT of less than three days favoured the production of acetic acid during the thermophilic (70 °C) processing of tofu wastewater. Moreover, microbial profiling studies showed that high HRTs promoted the growth of unwanted microorganisms, particularly *Methanothermobacter* species [202]. Moreover, Li et al. [203] revealed that the HRTs of 1–2 days are optimum for butyrate and acetate production when using whey as a feedstock. In another study, it was demonstrated that acetate and butyrate were the main by-products in a continuous stirred tank reactor when the HRT was maintained for 8 h [204]. Besides, acetate and butyrate accounted for more than 80% of the total metabolites [204]. Nevertheless, it should be noted that the attainment of the desired VFA type is not solely dependent on HRT; other process parameters should also be taken into consideration when regulating the HRT during acidogenic fermentation [18,205].

When analysing the effects of OLR on VFA production, Yun and Cho [206] observed that acetate and butyrate together with H_2 were the main by-products during the continuous acidogenic process. In the study by Yun and Cho [206], acetate and butyrate accounted for 38% and 50% of the total VFAs when the OLR was enhanced from 19 to 35 g COD/day. In addition, the study of the microorganisms which were prevalent during the process revealed that *Clostridium* and *Lactobacillus* species were the main VFA-producing microorganisms [206]. Wijekoon et al. [207] reported acetate, iso-butyrate, n-butyrate, propionate, and valerate as the main intermediate products in a two-stage thermophilic anaerobic membrane reactor. The authors also observed that increasing the OLR (5–12 kg COD/m³) altered the VFA profile from acetate to n-butyrate, and the total VFA content was also enhanced with increased OLR [207]. In another similar study that was conducted in a continuous membrane reactor, the propionate, butyrate, and isobutyric were the main by-products with concentrations of 1.1845, 0.5160, and 0.3580 mmol/L, respectively [208]. These intermediates were achieved at 550 and 715 mg COD_{feed} [208]. Elsewhere, it was demonstrated that varying OLR and HRT in the ranges of 0.8–11.0 g COD/L day and 108–15 days, respectively, had a profound effect on acidogenic communities during anaerobic digestion process [209]. Microbial characterization studies showed that Firmicutes was the most abundant phylum at low OLRs. At the genus level, *Clostridium* was the most dominant species. Other bacterial groups belonging to the phyla Bacteroidetes, Actinobacteria, and Gammaproteobacteria, were prevalent at high OLRs [209].

3.6. Hydrogen partial pressure

Researchers have realized that the H_2 partial pressure (also known as H_2 headspace) increases during the course of the acidogenic process and subsequently leads to low VFA yields [210,211]. This is caused by the reduction of ferredoxin (a membrane-bound protein which regulates the transfer of electrons) which is triggered during the process, resulting in the oxidation of H_2 to protons (Eq. (12)) which in turn produces a thermodynamically unstable process [212].

Furthermore, the increase in H_2 headspace shifts the metabolic activities towards inhibitory reactions such as lactate, ethanol, acetone and butanol pathways [213–215]. Therefore, it is crucial to maintain a low H_2 partial pressure during acidogenesis in order to enhance the concentrations of VFAs. In recent years, various innovative methods have been used to reduce the H_2 partial pressure during VFA production. For example, Zhou and co-authors [216] applied three strategies such as headspace removal, CO_2 sparging, and $H_2:CO_2$ (80:20) sparging, respectively, in order to reduce the H_2 partial pressure during the production of VFAs. Remarkably, all these methods had a positive effect on VFA production as evident by yields that were 1.04, 1.19, and 1.30-fold greater than that of the control experiment [216]. It was also demonstrated that the maintenance of low partial pressure favoured the proliferation of *Clostridium* species, which are prominent acidogenic-producing microorganisms [216]. These results are agreement with findings from other studies which show that low partial pressure stimulates the growth of hydrolytic and acidogenic bacteria during anaerobic digestion [217–219]. In another study, Mateos et al. [220] demonstrated that the CO_2 in the microbial electrosynthesis system (MES) could be enhanced by enriching the biofilm-forming microbial communities that are responsible for CO_2 sequestration. This was achieved by a continuous recirculation of the gas headspace through the catholyte which led to a remarkable 44% improvement in process performance. Moreover, a maximum acetate concentration of 1957 mg/L was attained during the MES process, with *Clostridium* and other species such as *Arcobacter*, *Desulfovibrio*, *Pseudomonas*, *Acinetobacter* and *Sporomusa* constituting the multispecies biofilms in the cathodic chamber [220]. On the contrary, Zhang et al. [221] studied the effects of H_2 partial pressure alongside other variables such as pH, temperature, and glucose on the thermophilic mixed fermentation process. It was shown that the effect of H_2 partial pressure was negligible but varying the pH from 4.0 to 7.0 changed the metabolite composition from acetate, butyrate, and H_2 to acetate, ethanol, propionate, and formate during the thermophilic microbial process [221]. The results from this study indicate clearly that the impact of other operational parameters should also be taken into consideration when regulating the H_2 partial pressure during VFA production.

3.7. Reactor types

In addition to the above-mentioned parameters, the types of reactors used in VFA production should not be overlooked as reactor design impacts the substrate conversion efficiency, mass transfer, prevailing microbial populations, and VFA yields during acidogenesis [222,223]. As highlighted earlier, most studies use continuously stirred tank reactors (CSTRs) in comparison to their batch and semi-fed counterparts. This is attributable to their ability to provide good mass transfer, which in turn leads to high concentrations of VFAs during fermentation [224–227]. Nonetheless, the major drawback that is associated with CSTRs is biomass washout. It has been reported in numerous acidogenic studies that biomass washout occurs when using these reactors at short HRTs, resulting in minimum VFA yields and unstable process performance [155,228,229]. In order to retain high biomass concentrations and consequently generate high VFA production, several approaches have been used in recent studies. These include the use of sludge

immobilization, reactor designs such as anaerobic-membrane reactor [208,230], anaerobic-sequencing batch reactor [231,232], fixed-bed reactor [233,234], fluidized-bed bioreactor [235,236], and upflow reactor [237,238].

3.8. Nanoparticles

The emergence of nanotechnology has opened up many avenues in the fields of biofuels and biocommodities in recent years due to the extensive application of nanomaterials in cosmetics, medicine, agriculture, pharmaceuticals, food, and electronics, to name the least [264–267]. The intrinsic and exquisite properties of nanoparticles allow them to be immobilized/attached in acidogenic-producing species during VFAs production. Moreover, their relatively small size ranging from 1 to 100 nm provides (i) a high-surface-area-to-volume-ratio thus enabling these molecules to react with many species during acidogenesis, (ii) fast reaction rates than their bulk counterparts, (iii) transfer of electrons during the process, and (iv) multispecies biofilm-forming communities within the reactor [268–270]. These nano-based materials are now being used in the recovery of VFAs in waste streams. Wei et al. [271] used zero-valent iron (Fe^0) nanoparticles for increasing the recovery of VFAs and CH_4 using an organic fraction of municipal solid waste (OFMSW) at a high organic loading rate (OLR). The use of Fe^0 nano-additives changed the composition of the VFA profile from butyric-type fermentation to propionate-type fermentation [271]. Iron is regarded as one of the most important nano-additives due to its enrichment role on the metabolic machinery of acidogenic species such as *Clostridium* sp., which are the dominant acidogenic-regulating microorganisms, as shown in Fig. 5 [264,272,273]. Blanchette et al. [274] reported that immobilizing hydrolytic enzymes like cellulases on nanospheres could be instrumental in the degradation of plant-derived cellulose, which in turn could be used in biofuel production processes. The cellulase enzymes obtained from the *Aspergillus fumigatus* were treated with zinc oxide nanoparticles to strengthen the thermal and pH stability of these enzymes. In another study, it was also observed that the use of silver nanoparticles prolonged the acidogenic process by enriching the acidogenic-producing bacterial species [275]. This approach was advantageous because it successfully retained the optimum pH of 5.0–7.0 during the fermentation process [275]. Other types of nano-based materials such as nanocomposites ($Si@CoFe_2O_4$ and Fe_3O_4 /alginate) and graphene-based nanomaterials have also been exploited in the enrichment of acidogenic pathways [276,277]. Therefore, it is evident from these results that nanoparticles could play a pivotal role in the recovery of VFAs from acidogenic effluents and other related waste streams.

4. Other emerging value-added compounds in the valorization of organic wastes

In addition to the compounds that are produced in Section 2, this chapter examines the bioprocesses that can be integrated with dark fermentation for the production of other valuable compounds. Due to a wide variety of products that are being produced in biorefinery concepts, this section focuses primarily on those compounds that can be simultaneously produced with H_2 or produced in secondary fermentation processes.

4.1. Citric acid

Citric acid is a natural weak organic acid produced mainly by *Aspergillus niger* [279,280]. There has recently been an increase in citric acid demand due to its diverse use in cosmetics, foods, beverages, chemicals, and pharmaceuticals [281,282]. More than 2 million tons of citric acid is produced each year, and it is estimated to have an annual growth rate of 4% [283]. However, the use of pure sugars such as glucose continues to escalate the costs of this process [284]. Hence, a

Fig. 5. The role of Fe^0 nanoparticles on acidogens. Reprinted from Ref. [278], with permission from Elsevier.

major focus directed towards the use of cheap substrates has led to reduced costs associated with this product. A review by Show et al. [282] summarized the types of organic wastes that can be used in citric acid fermentation. During the downstream process, the spent medium can be incorporated into a biorefinery framework and be used in the synthesis of other valuable bioproducts such as biomethane [285] and biohydrogen [286,287]. Alternatively, the effluents from other bioprocesses can be used in citric acid production [288].

4.2. Succinic acid

Succinic acid is another platform molecule that is used as a precursor for many chemicals, including adipic acid, 1,4-butanediol, tetrahydrofuran, γ -butyrolactone, succinonitrile, succinimide, 4,4-bionolle, and various pyrrolidones [289,290]. This compound has a production capacity of more than 30 000 per year, which corresponds to a market value of \$125 million [291]. The biocatalytic route has attracted a lot of attention in the last decade due to its low energy consumption and waste beneficiation capabilities [292]. A wide variety of microorganisms and inoculum sources have been explored in succinic acid fermentation [293], which makes it easier for this process to be integrated with other fermentation processes. In a biorefinery context, it has been shown that this biomolecule can be simultaneously produced with other biofuels such as biohydrogen [294], biogas [295], and bioethanol [296], and this holds a huge potential in the valorization of VFAs from various waste streams.

4.3. Butanol

Butanol is an ethyl alcohol that is mainly used as a chemical intermediate, solvent, and extractant in various commercial applications such as cosmetics and pharmaceutical industries and also used in the production of other chemicals such as butyl acrylate and methacrylate [297,298]. It consists of four isomeric structures, namely the n-butanol ($\text{n-C}_4\text{H}_9\text{OH}$), sec-butanol ($\text{sec-C}_4\text{H}_9\text{OH}$), iso-butanol ($\text{iso-C}_4\text{H}_9\text{OH}$), and tert-butanol ($\text{tert-C}_4\text{H}_9\text{OH}$) [299,300]. It is commercially produced using petroleum-based technologies [301]. To make a transition from these environmentally and human-threatening processes, scientists developed the acetone-butanol-ethanol fermentation route around the late 1800s and early 1900s [302,303], which traditionally used first-generation feedstocks like corn, cassava, sugarcane or wheat [304,305]. However, this process is still hindered by the low butanol yields and the high process costs [306,307]. Thus, recent studies are now using biomass residues (agricultural wastes, lignocellulosic wastes, and industrial wastes) alongside the cellulosic microbes found in various habitats to curb the process costs and pave the way for scale-up studies [308–310]. Zhang et al. [297] recently used an amylolytic *Clostridium* species to produce butanol and hydrogen from food waste simultaneously. It was also shown that the supplementation of calcium ions increased the butanol yield by more than 17.7% because these additives enhanced the amylase activity [298]. Similarly, Cao et al. [311] observed that the co-valorization of corn steep liquor (CSL) and paper mill sludge (PMS) resulted in higher butanol production. The CSL did not only serve as a nitrogen source but supplied the essential lactic acid

that was utilized by *Clostridium tyrobutyricum*, thereby enhancing the production of butanol. These studies offer a promising approach to solving environmental issues and energy scarcity.

4.4. Biofertilizers

The exploitation of digestates as biofertilizers is gaining a lot of prominence in the agricultural sector due to their potential role in food safety and sustainable crop production as opposed to commercial soil management methods which primarily relies on chemical-based fertilizers, which in turn pose a serious threat to humans and the environment [312,313]. The digestates (anaerobically digested slurry) are used as biofertilizers because they contain various nutrients such as nitrogen, magnesium, phosphorous, and potassium [314]. They have also been shown to contain different plant growth-promoting microorganisms such as nitrogen-fixing bacteria and phosphate-solubilizing bacteria [315,316]. According to Ahemad and Kibret [316], these microorganisms facilitate plant-growth by (i) stimulating the plant-growth hormones, (ii) inhibiting pathogens, and (iii) enhancing nutrient and water uptake in plants. Khayum et al. [314] evaluated the possibility of using an anaerobically digested spent tea as a biofertilizer. It was observed that this digestate could be used as a biofertilizer as it contained various micronutrients such as nitrogen, phosphorous, and potassium after the anaerobic digestion process [314]. Owamah et al. [317] reported that the digestate consisted of various beneficial microorganisms such as *Aspergillus*, *Bacillus*, *Klebsiella*, *Penicillium* and *Pseudomonas* which boosts the efficiency of the biofertilizer through nitrogen-fixation and nutrient solubility in soils. Therefore, biofertilizers that are derived from digestates may increase the crop-yields and reduce the use of toxic chemicals in the agricultural sector. However, more research is needed to understand the long-term effects of digestates on soil microbiota, nutrient, and salts accumulation [318]. This will in turn provide the best practices for the applications of these digestates in irrigation systems [318].

5. Current status, opportunities and prospects for dark fermentation-based biorefinery

Dark fermentation-based biorefinery concepts are now being explored by researchers at laboratory-scale in efforts to produce diverse bio-based products [319–322]. The full-scale demonstrations show an improvement in technology readiness level (TRL) for these biorefinery systems. A full-scale study showed the production of VFAs from sewage sludge, and these intermediates were later used as a carbon source for improving biological nitrogen and phosphorus removal in wastewater treatment plant [149]. The use of fermented liquids produced an efficiency that is similar to that of a commercial acetic acid process and generated removal efficiencies of 72.39% and 89.65% for nitrogen and phosphorus [149]. A pilot-scale study showed that cellulosic primary sludge could be used as a carbon source for VFAs production [323]. An optimal VFA yield of 2.57 kg COD/m³.d was achieved at operational pH of 9.0 and hydraulic retention time of 6 days under mesophilic conditions [323]. Elsewhere, wastewater from the paper industry was used as a substrate for PHA production in a pilot-scale process. The plant was designed as a three-stage process comprising of (i) anaerobic fermentation for enhancement of VFAs, (ii) enrichment of PHA-producing species, and (iii) accumulation of PHA in the form of biomass [324]. A maximum PHA content of 0.70–0.80 g PHA/g VSS was achieved at the end of the anaerobic process. Microbial analysis showed that *Plasticumulans acidivorans* was the most dominant species during the process [324].

In other acidogenic-based biorefinery processes, researchers demonstrated the production of valuable compounds such as omega-3 fatty acids using VFAs that are obtained from the dark fermentation effluents. In this technology, the VFAs are biotransformed into omega-3 fatty acids using potent microalgal species such as *Cryptocodinium cohnii* [322,325]. Other strains such as *Aurantiochytrium* sp.,

Schizochytrium sp., *Thraustochytrium* sp., and *Ulkenia* sp. can also be incorporated into dark fermentation-based biorefinery because they can produce diverse valuable compounds including omega-3 oils, biodiesel, and exopolysaccharides [322].

Some existing pilot-scale demonstrations of the biorefinery-based plants that can be integrated with dark fermentation processes are depicted in Table 4. Fig. 6 shows a biorefinery framework involving dark fermentation with other biochemical processes. The biorefinery approach is classified into first-, second- and third-generation, depending on the types of feedstocks used. The feedstocks in the first-generation biorefineries come from surplus food crops or crops that are grown using advanced agricultural technologies. The feedstock for second-generation biorefineries involves residual biomass such as food waste, agro-industrial residues, as well as liquid effluents. These types of substrates are biodegradable in nature and also includes feedstocks such as food waste, cheese whey, wastewaters from beverage industries, and lignocellulosic materials such as rice straw, wheat straw, and corn stalk which requires some degree of pretreatment in order to release the fermentable sugars. Third-generation biorefineries usually rely on feedstocks like microalgae [326].

In addition, Fig. 7 summarizes the number of articles that have been published in the area of biorefinery. Herein, scientists use various integrated technologies to produce multiple compounds using organic wastes and various microorganisms, as mentioned earlier. The number of research articles on this topic is increasing, and this will ultimately boost the development of clean technologies. Although these studies do not focus solely on dark fermentation-based biorefinery, it is hoped that some of the novel methods applied in these studies could also be adopted in acidogenic biorefineries to advance this process.

In summary, the future prospects for dark fermentation-based biorefineries look promising. The global production capacity for VFAs in 2013 was estimated at 2.9 million tons, and this corresponded to a

Table 4
Pilot-scale demonstrations of biorefinery-based processes.

Company (Country)	Feedstock	Product	Capacity (tons)	Reference
DuPont (USA)	Corn Stover	Ethanol	300 000	[329]
NatureWorks (USA)	Corn, cassava, sugarcane	Biopolymers	75 000–150 000	[330]
Futero Green	–	Biopolymers	1500	
Biorefinery Utzenaich (Austria)	Grass silage	Biogas, electricity, heat, lactic acid, amino acid, biomaterials, fertilizer	20 000–40 000	[331]
Biorefinery Lenzing (Austria)	Wood	Furfural, cellulosic fibres, acetic acid, artificial sweetener	25 000	[332]
Lignol Innovations Ltd. (Canada)	Wood, straw, energy crops	Cellulosic ethanol, lignin, specialty cellulose, acetic acid, lignin, furfural, sugars	–	[333]
Bumaga pilot plant (Netherlands)	Wastewater	Fatty acids	–	[334]
Algenol (USA)	Algae	Ethanol, gasoline, jet fuel, diesel	–	[335]
Australian Renewable Fuels Ltd (Australia)	Low grade animal fats, waste vegetable oils	biodiesel, biogas, burner fuel, glycerine, sulphated potash	–	[326]

–: unknown.

Fig. 6. Dark fermentation-based biorefinery system. Adapted and modified from Cherubini et al. [336].

Fig. 7. Number of published articles on biorefineries [337].

market value of 3.5 billion US dollars. These compounds are also expected to have an annual growth rate of 8.8% until 2023 [327]. The fatty acids market has experienced a significant growth in the last decade due to the increasing demands for these metabolites as they are used in various sectors such as pharmaceuticals, food, beverages, cosmetics, and detergents [327]. Likewise, the biopolymers have a market growth rate of 9–30% per annum and expected to have a high production capacity in the next coming years [328].

6. Conclusions and recommendations

In recent years, a lot of research has been geared towards integrating dark fermentation with other biotechnological processes in order to improve the energetic gains from this process and also harness other valuable compounds from bio-based technologies. In comparison to a single bioprocess, integrated bioprocesses via the use of novel technologies to produce multiple compounds based on the biorefinery framework have several benefits such as (i) complete conversion of acidogenic-derived VFAs and other waste streams into valuable compounds, (ii) minimization of the operating costs during the downstream

process, (iii) synergistic relationships between different biotechnological processes, (iv) generating multiple products, and (v) minimization of wastes after the downstream process.

This review highlights the use of VFAs that are derived from the dark fermentation process. It also discusses the parameters that are applied to enhance the recovery of VFAs from these acidogenic effluents and other related waste streams. Furthermore, it elucidates the use of novel methods such as nano-additives/nanoparticles, which could potentially be used to optimize the recovery of these valuable compounds. The work also discusses the advances in dark fermentation-based biorefinery, particularly the development of pilot-scale systems. However, the use of acidogenic-derived VFAs as precursors in biotechnological processes is relatively new in the field of biorefinery. To advance the utilization of acidogenic-derived VFAs in biorefineries, several suggestions are proposed for future studies. These include (i) gaining deeper insights into the process variables that enhance the VFAs-producing microorganisms during the acidogenic process, (ii) finding optimal feedstocks and inoculum sources (preferable mixed cultures from diverse habitats) which could improve the extraction of these compounds during the anaerobic process, and (iii) conducting large-scale biorefinery processes in order to truly understand the process dynamics and process conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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