Renewable and Sustainable Energy Reviews 143 (2021) 110971

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: http://www.elsevier.com/locate/rser

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

ARTICLE INFO

Keywords:
Acidogenic-derived VFAs
Dark fermentation
Biofuels
Biocommodities

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 H_2-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 H_2 production is still affected by various process

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

https://doi.org/10.1016/j.rser.2021.110971
Received 2 May 2020; Received in revised form 8 March 2021; Accepted 12 March 2021
Available online 24 March 2021

Nomenclature

Abbreviations

COD	chemical oxygen demand
DCW	dry cell weight
HRT	hydraulic retention time
MECs	microbial electrolysis cells
MFCs	microbial fuel cells
OFSMW	organic fraction of solid municipal waste
OLR	organic loading rate
PHAs	polyhydroxyalkanoates
TVS	total volatile solids
VFAs	volatile fatty acids
VS	volatile solids
VSS	volatile suspended solids

Units

d	day
g	gram
h	hour
Kg	kilogram
L	litre
mg	milligram
mL	millilitre
mol	mol amount
t	time

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 H_2-scavenging reactions which consume the desired H_2 [12]. Secondly, the organic feedstocks must undergo vigorous pretreatment stages before the acidogenic process (the main dark fermentative H_2-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 H_2-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 CO_2 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	*Pseudomonas otitidis*	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	*Serratia ureilytica*	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	*Pseudomonas chlororaphis* 555	Batch	6.9	30	16–18	0.52 g/g substrate	Ruiz et al. [49]
Growth medium	*Pseudomonas putida* Bet001	Batch	6.8	30	48	–	Razaif-Mazinah et al. [50]
Growth medium	*Delftia tsuruhatensis* 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 H_2-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 H_2 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 biofuels 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 H_2 and VFAs) are converted into CH_4 (50–70%), CO_2 (25–45%) and other traceable compounds such as H_2S, and NH_3 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 CH_4 (CH_4>94%) through the CO_2-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	*Clostridium thermosaccharolyticum*	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 Propionate	Zhang et al. [139]
Mushroom waste	Anaerobic sludge	Batch reactor	8.0	55	–	–	Acetate Butyrate Propionate Valeric acid	Lay et al. [140]
Sucrose	Anaerobic sludge	Batch reactor	8.95	35	–	–	Butyrate Propionate	Choi and Ahn [141]
Synthetic medium	Dewatered sludge	Semi-continuous reactor	6.6–7.1	55	–	–	Acetate Butyrate Propionate Valerate	Hao and Wang [148]
Waste activated sludge	–	Batch reactors	8.0–9.0	35, 55	–	–	Acetate Propionate Valerate	Zhang et al. [150]
Wastewater	Activated sludge	Semi-continuous reactor	10–11	19–25	14.9	21 day	Acetate Butyrate Propionate Valerate	Liu et al. [149]
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 Lactate	Infantes et al. [245]
Organic waste	Compost	CSTR	6.5	37	20–30	10.8 g COD/L.d	Acetate Butyrate Propionate	Khanal et al. [246]
Food waste	Seed culture	CSTR	>4.0	37	12	6 g/L	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]
Macrocystis pyrifera 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 Lactate	Rosa et al. [253]
Cheese whey	Granular sludge	UASBR	5.3–5.5	35	13–8	20–30 g COD/L. day	Acetate Butyrate Propionate	Carrillo-Reyes et al. [254]
Sugarcane vinasse	Anaerobic sludge	AFBR	4.0–5.0	22	6	5 g COD/L	Butyrate Propionate	dos Reis et al. [255]
Glycerol waste	*Enterobacter aerogenes* 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/m^2 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/m^2 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

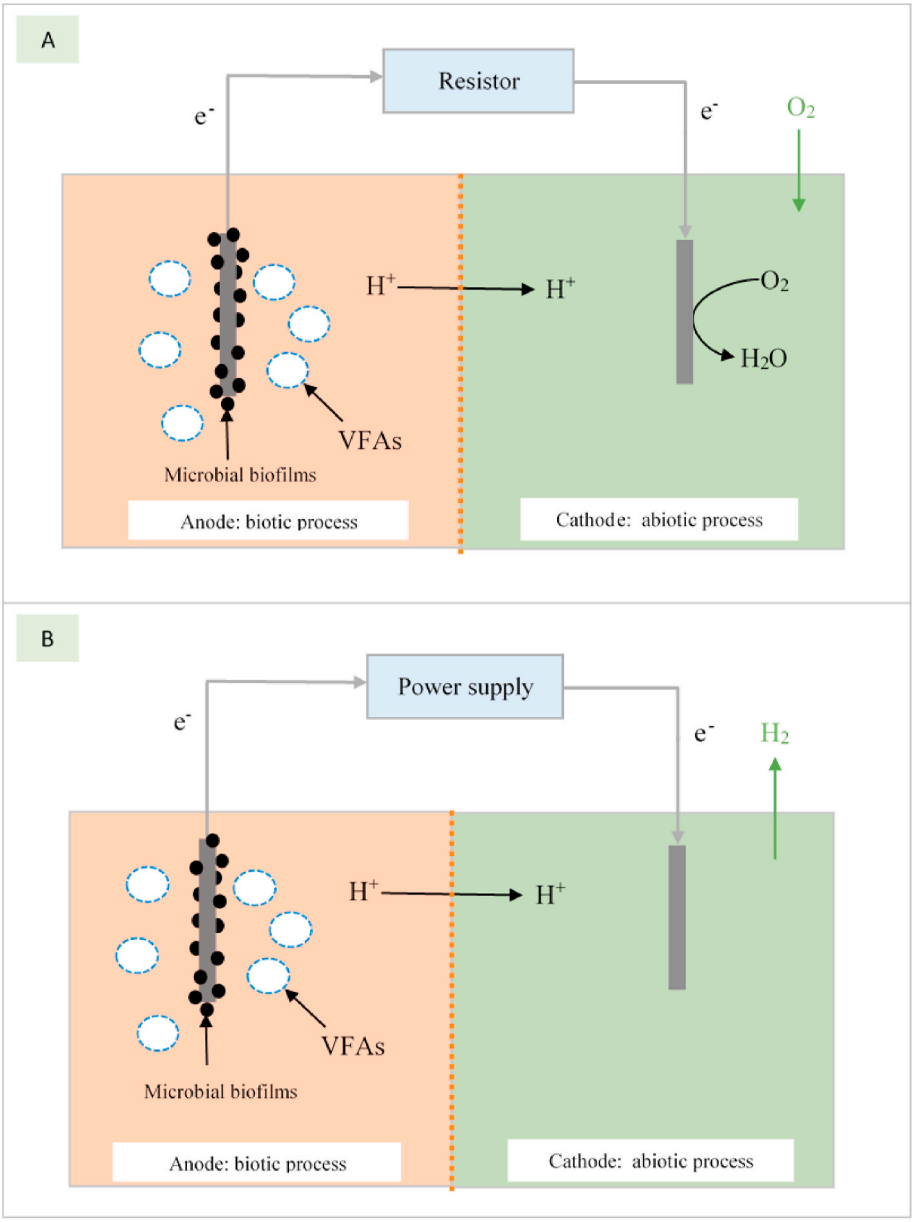

Fig. 1. Acidogenic-derived VFAs used in a microbial fuel cell (A) and microbial electrolysis cell (B). Adapted and modified from Du et al. [84].

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].

$$\text{Anode}: CH_3COO + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e \quad (1)$$

$$\text{Cathode}: O_2 + 4e + 4H^+ \rightarrow 2H_2O \quad (2)$$

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 *Rhodobacter* 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 bioelectrochemical 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].

$$\text{Anode}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^- \quad (3)$$

$$\text{Cathode}: 8H^+ + 8e^- \rightarrow 4H_2 \quad (4)$$

$$Cu \rightarrow Cu^{2+} + 2e^- \quad (5)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (6)$$

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 CO_2 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 H_2 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.

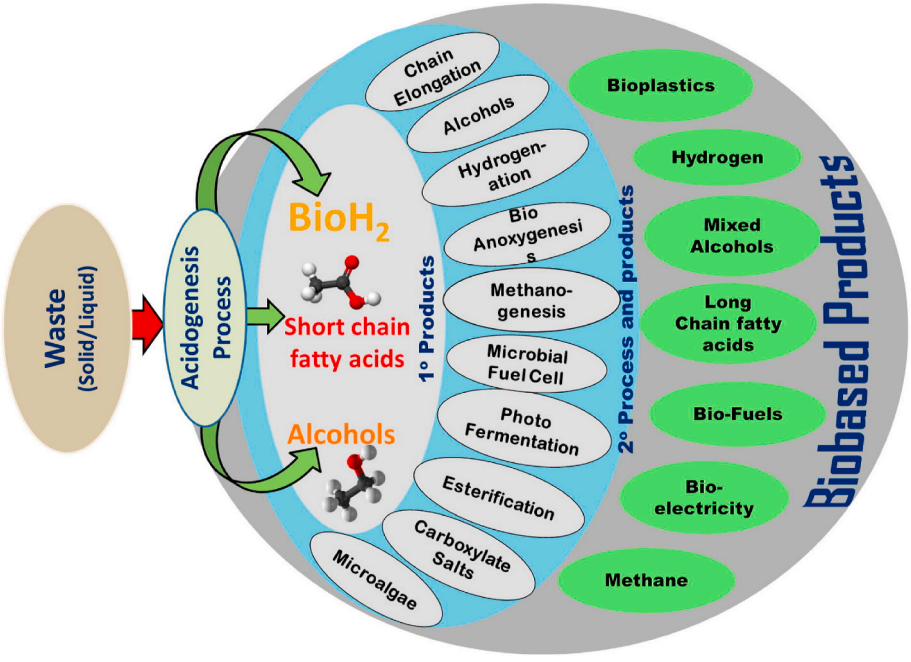

Fig. 2. A schematic diagram illustrating the integration of dark fermentation with other biotechnological processes. Reprinted from Ref. [30], with permission from Elsevier.

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.-4.5%) 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 VAFs 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

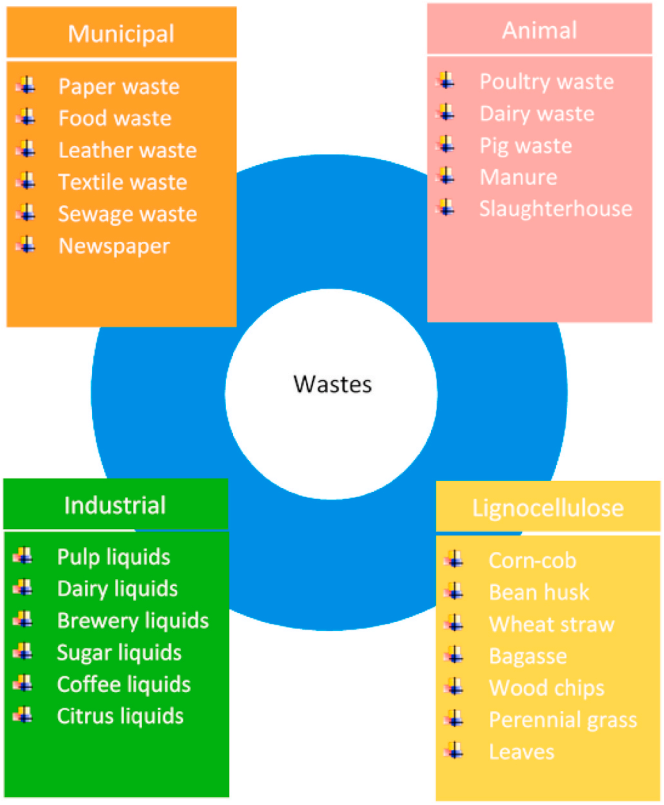

Fig. 3. Biomass residues used in VFAs production. Adapted and modified from Rehan et al. [176].

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 H_2 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 H_2 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).

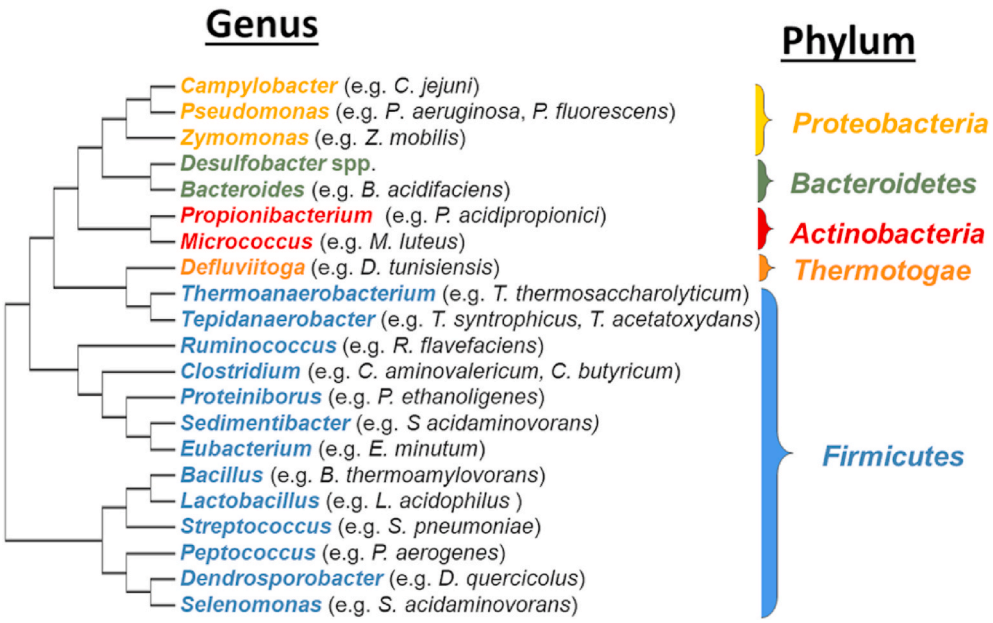

Fig. 4. The 16S rRNA gene-based tree showing the relatedness of acidogenic-producers.

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].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (7)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (8)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad (9)$$

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH + 2CO_2 \quad (10)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2OH + H_2O + CH_3COOH + 2CO_2 + 2H_2 \quad (11)$$

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 bioprocesses [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/m^3) 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].

$$Fd_{ox} + H_2 \rightarrow F_{red} + 2H^+ \quad (12)$$

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 reacts 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

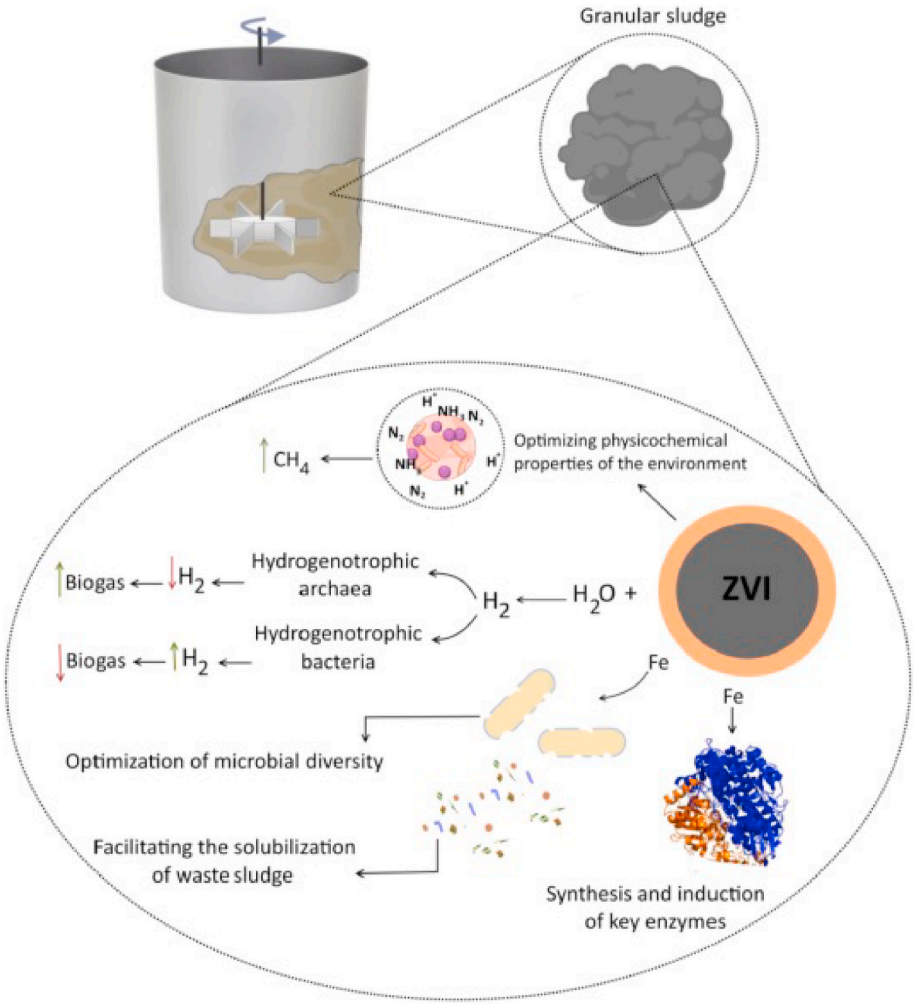

Fig. 5. The role of Fe^0 nanoparticles on acidogens. Reprinted from Ref. [278], with permission from Elsevier.

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 (n-C_4H_9OH), sec-butanol (sec-C_4H_9OH), iso-butanol (iso-C_4H_9OH), and tert-butanol (tert-C_4H_9OH) [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/m^3.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 *Plasticicumulans 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 *Crypthecodinium 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]
Futerro	–	Biopolymers	1500	
Green 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, speciality 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.

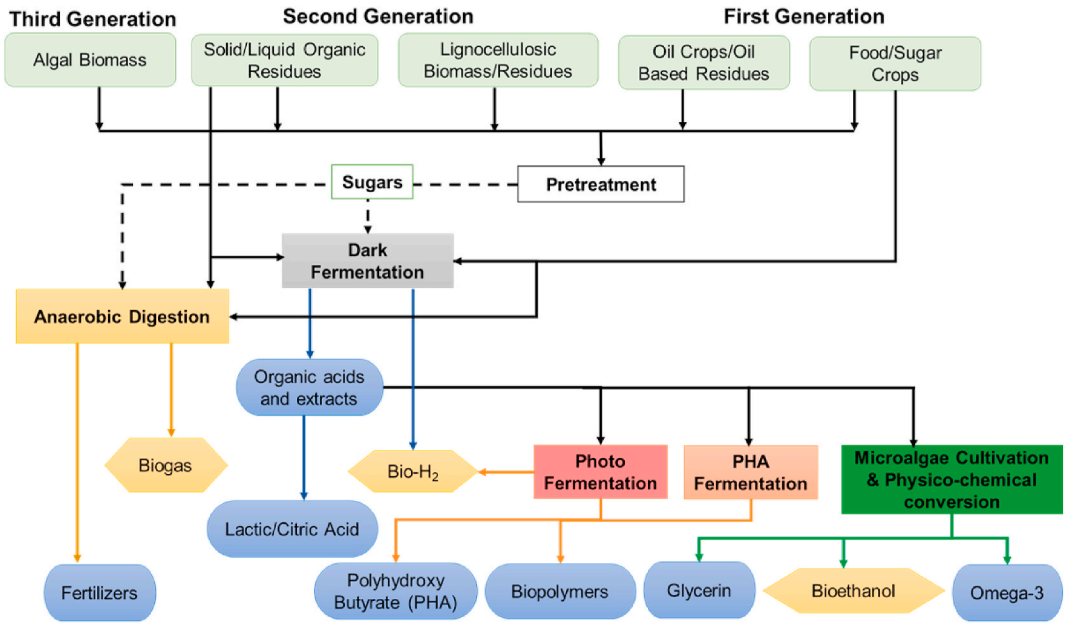

Fig. 6. Dark fermentation-based biorefinery system. Adapted and modified from Cherubini et al. [336].

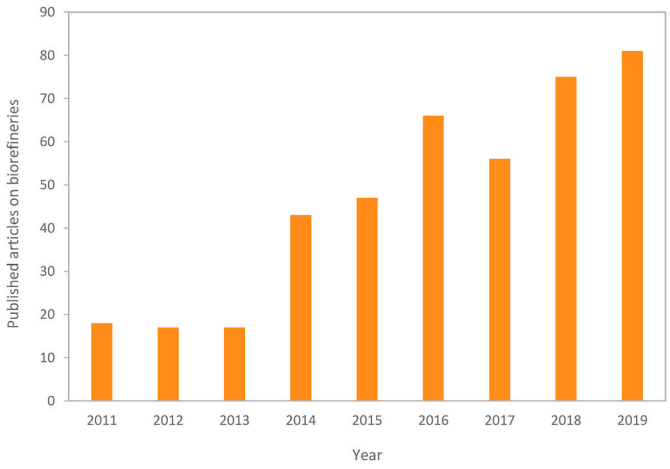

Fig. 7. Number of published articles on biorefineries [337].

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.

References

[1] UN Environment Programme. Soild waste management. https://www.unenvironment.org/explore-topics/resource-efficiency/what-we-do/cities/solid-waste-management. [Accessed 17 February 2020].
[2] Sekoai PT, Yoro KO, Daramola MO. Batch fermentative biohydrogen production process using immobilized anaerobic sludge from organic solid waste. Environments 2016;3:38.
[3] Abdel-Shafya HI, Mansour MSM. Solid waste issue: sources, composition, disposal, recycling, and valorization. Egypt J Pet 2018;27:1275–90.
[4] Arancon RAD, Lin CSK, Chan KM, Kwan TH, Luque R. Advances on waste valorization: new horizons for a more sustainable society. Energy Sci Eng 2013;1:53–71.

[5] Atasoy M, Owusu-Agyeman I, Plaza E, Cetecioglu Z. Bio-based volatile fatty acid production and recovery from waste streams: current status and future challenges. Bioresour Technol 2018;268:773–86.
[6] Strazzera G, Battista F, Garcia NH, Frison N, Bolzonella D. Volatile fatty acids production from food wastes for biorefinery platforms: a review. J Environ Manag 2018;226.
[7] Mata TM, Martins AA, Caetano NS. Bio-refinery approach for spent coffee grounds valorization. Bioresour Technol 2018;247:1077–84.
[8] Soares JF, Confortin TC, Todero I, Mayer FD, Mazutti MA. Dark fermentative biohydrogen production from lignocellulosic biomass: technological challenges and future prospects. Renew Sustain Energy Rev 2020;117:109484.
[9] Ebrahimian F, Karimi K. Efficient biohydrogen and advanced biofuel coproduction from municipal solid waste through a clean process. Bioresour Technol 2020;300:122656.
[10] Banu JR, Kavitha S, Kannah RY, Bhosale RR, G K. Industrial wastewater to biohydrogen: possibilities towards successful biorefinery route. Bioresour Technol 2020;298:122378.
[11] Show K-Y, Yan Y, Zong C, Guo N, Chang J-S, Lee D-J. State of the art and challenges of biohydrogen from microalgae. Bioresour Technol 2019;289:121747.
[12] Preethi, Usman MTM, Banu JR, Gunasekaran M, Kumar G. Biohydrogen production from industrial wastewater: an overview. Bioresour Technol Rep 2019;7:100287.
[13] Nagarajan D, Chang J-S, Lee D-J. Pretreatment of microalgal biomass for efficient biohydrogen production - recent insights and future perspectives. Bioresour Technol 2020;302:122871.
[14] Sekoai PT. Modelling and optimization of operational setpoint parameters for maximum fermentative biohydrogen production using Box-Behnken design. Fermentatio 2016;2:15.
[15] Tapia-Venegas E, Ramirez-Morales JE, Silva-Illanes F, Toledo-Alarcón J, Paillet F, Escudie R, et al. Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. Rev Environ Sci Biotechnol 2015;14:761–85.
[16] Sekoai PT, Yoro KO, Bodunrin MO, Ayeni AO, Daramola MO. Integrated system approach to dark fermentative biohydrogen production for enhanced yield, energy efficiency and substrate recovery. Rev Environ Sci Biotechnol 2018;17:501–29.
[17] Woo HC, Kim YH. Eco-efficient recovery of bio-based volatile C2–6 fatty acids. Biotechnol Biofuels 2019;12:92.
[18] Kumar G, Ponnusamy VK, Bhosale RR, Shobana S, Yoon J-J, Bhatia SK, et al. A review on the conversion of volatile fatty acids to polyhydroxyalkonates using dark fermentative effluents from hydrogen production. Bioresour Technol 2019:121427.
[19] Dahiya S, Sarkar O, Swamy YV, Mohan SV. Acidogenic fermentation of food waste for volatile fatty acid production with co-generation of biohydrogen. Bioresour Technol 2015;182:103–13.
[20] El-Mansi EMT, Bryce CFA, Demain AL, Allman AR. Fermentation microbiology and biotechnology. third ed. Boca Raton: CRC Press; 2011. p. 555.
[21] Plastemart. http://www.plastemart.com/upload/literature/global-acetic-acid-market-estimated-15.5-million-tons-2020.asp. [Accessed 17 February 2020].
[22] Dwidar M, Park J-Y, Mitchell RJ, Sang B-I. The future of butyric acid in industry. Sci World J 2012;2012:471417.
[23] Xiao Z, Cheng C, Bao T, Liu L, Wang B, Tao W, et al. Production of butyric acid from acid hydrolysate of corn husk in fermentation by *Clostridium tyrobutyricum*: kinetics and process economic. Biotechnol Fuels 2018;11:164.
[24] Du G, Liu L, Chen J. White biotechnology for organic acids. In: Pandey A, Höfer R, Taherzadeh M, Nampoothiri M, Larroche C, editors. Industrial biorefineries and white biotechnology. first ed. Elsevier; 2015. p. 400–44.
[25] Ghaffar T, Irshad M, Anwar Z, Aqil T, Zulifqar Z, Tariq A, et al. Recent trends in lactic acid biotechnology: a brief review on production to purification. J Radiat Res Appl Sci 2014;7:222–9.
[26] Ahmadi N, Khosravi-Darani K, Mortazavian AM. An overview of biotechnological production of propionic acid: from upstream to downstream processes. Electron J Biotechnol 2017;28:67–75.
[27] !!! INVALID CITATION !!! [22,23].
[28] Mülhaupt R. Green polymer chemistry and bio-based plastics: dreams and reality. Macromol Chem Phys 2012;214:159–74.
[29] Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. J Hazard Mater 2018;344:179–99.
[30] Mohan SV, Nikhil G, Chiranjeevi P, Reddy CN, Rohit M, Kumar AN, et al. Waste biorefinery models towards sustainable circular bioeconomy: critical review and future perspectives. Bioresour Technol 2016;215:2–12.
[31] Sambusiti C, Bellucci M, Zabaniotou A, Beneduce L, Monlau F. Algae as promising feedstocks for fermentative biohydrogen production according to a biorefinery approach: a comprehensive review. Renew Sustain Energy Rev 2015;44:20–36.
[32] Islam MK, Wang H, Rehman S, Dong C, Hsu H-Y, Lin CSK, et al. Sustainability metrics of pretreatment processes in a waste derived lignocellulosic biomass biorefinery. Bioresour Technol 2020;298:122558.
[33] Chandrasekhar K, Kumar S, Lee B-D, Kim S-H. Waste based hydrogen production for circular bioeconomy: current status and future direction. Bioresour Technol 2020;302:122920.
[34] Bátori V, Åkesson D, Zamani A, Taherzadeh MJ, Horváth IS. Anaerobic degradation of bioplastics: a review. Waste Manag 2018;80:406–13.
[35] Thakur S, Chaudhary J, Sharma B, Verma A, Tamulevicius S, Thakur VK. Sustainability of bioplastics: opportunities and challenges. Curr Opin Green Sust Chem 2018;13:68–75.
[36] Chinaglia S, Tosin M, Degli-Innocenti F. Biodegradation rate of biodegradable plastics at molecular level. Polym Degrad Stabil 2018;147:237–44.
[37] Song J, Murphy R, Narayan R, Davies G. Biodegradable and compostable alternatives to conventional plastics. Philos Trans R Soc B: Biol Sci 2009;364:2127–39.
[38] Amulya K, Jukuri S, Mohan SV. Sustainable multistage process for enhanced productivity of bioplastics from waste remediation through aerobic dynamic feeding strategy: process integration for up-scaling. Bioresour Technol 2015;188:231–9.
[39] Kourmentza C, Ntaikou I, Lybertos G, Kornaros M. Polyhydroxyalkanoates from *Pseudomonas* sp. using synthetic and olive mill wastewater under limiting conditions. Int J Biol Macromol 2015;74:202–10.
[40] Du C, Sabirova J, Soetaert W, Lin SKC. Polyhydroxyalkanoates production from low-cost sustainable raw materials. Curr Chem Biol 2012;6:14–25.
[41] Mannina G, Presti D, Montiel-Jarillo G, Carrera J, Suárez-Ojeda ME. Recovery of polyhydroxyalkanoates (PHAs) from wastewater: a review. Bioresour Technol 2020;297:122478.
[42] Chen H, Meng H, Nie Z, Zhang M. Polyhydroxyalkanoate production from fermented volatile fatty acids: effect of pH and feeding regimes. Bioresour Technol 2013;128:533–8.
[43] Reddy CSK, Ghai R, Rashmi Kalia VC. Polyhydroxyalkanoates: an overview. Bioresour Technol 2003;87:137–46.
[44] Valentino F, Morgan-Sagastume F, Campanari S, Villano M, Werker A, Majone M. Carbon recovery from wastewater through bioconversion into biodegradable polymers. N Biotech 2017;37:9–23.
[45] Amaro TMMM, Rosa F, Comi G, Iacumin L. Prospects for the use of whey for polyhydroxyalkanoate (PHA) production. Front Microbiol 2019;10:992.
[46] Reddy MV, Mohan SV. Influence of aerobic and anoxic microenvironments on polyhydroxyalkanoates (PHA) production from food waste and acidogenic effluents using aerobic consortia. Bioresour Technol 2012;103:313–21.
[47] Venkateswar Reddy M, Kotamraju A, Venkata Mohan S. Bacterial synthesis of polyhydroxyalkanoates using dark fermentation effluents: comparison between pure and enriched mixed cultures. Eng Life Sci 2015;15:646–54.
[48] Albuquerque M, Martino V, Pollet E, Avérous L, Reis M. Mixed culture polyhydroxyalkanoate (PHA) production from volatile fatty acid (VFA)-rich streams: effect of substrate composition and feeding regime on PHA productivity, composition and properties. J Biotechnol 2011;151:66–76.
[49] Ruiz C, Kenny ST, Narancic T, Babu R, O'Connor K. Conversion of waste cooking oil into medium chain polyhydroxyalkanoates in a high cell density fermentation. J Biotechnol 2019;306:9–15.
[50] Razaif-Mazinah MRM, Anis SNS, Harun HI, Rashid KA, Annuar MSM. Unusual poly (3-hydroxyalkanoate)(PHA) biosynthesis behavior of *Pseudomonas putida* Bet001 and *Delftia tsuruhatensis* Bet002 isolated from palm oil mill effluent. Biotechnol Appl Biochem 2017;64:259–69.
[51] Riedel SL, Jahns S, Koenig S, Bock MC, Brigham CJ, Bader J, et al. Polyhydroxyalkanoates production with Ralstonia eutropha from low quality waste animal fats. J Biotechnol 2015;214:119–27.
[52] Beccari M, Bertin L, Dionisi D, Fava F, Lampis S, Majone M, et al. Exploiting olive oil mill effluents as a renewable resource for production of biodegradable polymers through a combined anaerobic–aerobic process. J Chem Technol Biotechnol 2009;84:901–8.
[53] Ntaikou I, Peroni CV, Kourmentza C, Ilieva V, Morelli A, Chiellini E, et al. Microbial bio-based plastics from olive-mill wastewater: generation and properties of polyhydroxyalkanoates from mixed cultures in a two-stage pilot scale system. J Biotechnol 2014;188:138–47.
[54] Morgan-Sagastume F, Hjort M, Cirne D, Gérardin F, Lacroix S, Gaval G, et al. Integrated production of polyhydroxyalkanoates (PHAs) with municipal wastewater and sludge treatment at pilot scale. Bioresour Technol 2015;181:78–89.
[55] Reddy MV, Nikhil G, Mohan SV, Swamy Y, Sarma P. *Pseudomonas otitidis* as a potential biocatalyst for polyhydroxyalkanoates (PHA) synthesis using synthetic wastewater and acidogenic effluents. Bioresour Technol 2012;123:471–9.
[56] Mohan SV, Reddy MV, Subhash GV, Sarma P. Fermentative effluents from hydrogen producing bioreactor as substrate for poly (β-OH) butyrate production with simultaneous treatment: an integrated approach. Bioresour Technol 2010;101:9382–6.
[57] Bengtsson S, Pisco AR, Reis MA, Lemos PC. Production of polyhydroxyalkanoates from fermented sugar cane molasses by a mixed culture enriched in glycogen accumulating organisms. J Biotechnol 2010;145:253–63.
[58] Morgan-Sagastume F, Valentino F, Hjort M, Cirne D, Karabegovic L, Gerardin F, et al. Polyhydroxyalkanoate (PHA) production from sludge and municipal wastewater treatment. Water Sci Technol 2014;69:177–84.
[59] Bo T, Zhu X, Zhang L, Tao Y, He X, Li D, et al. A new upgraded biogas production process: coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. Electrochem Commun 2014;45:67–70.
[60] Goswami R, Chattopadhyay P, Shome A, Banerjee SN, Chakraborty AK, Mathew AK, et al. An overview of physico-chemical mechanisms of biogas production by microbial communities: a step towards sustainable waste management. 3 Biotech 2016;6:72.
[61] Prussi M, Padella M, Conton M, Postma E, Lonza L. Review of technologies for biomethane production and assessment of Eu transport share in 2030. J Clean Prod 2019;222:565–72.

[62] Demirel B, Scherer P. Production of methane from sugar beet silage without manure addition by a single-stage anaerobic digestion process. Biomass Bioenergy 2008;32:203–9.
[63] Pramanik SK, Suja FB, Porhemmat M, Pramanik BK. Performance and kinetic model of a single-stage anaerobic digestion system operated at different successive operating stages for the treatment of food waste. Processes 2019;7:600.
[64] Bolzonella D, Battista F, Cavinato C, Gottardo M, Micolucci F, Lyberatos G, et al. Recent developments in biohythane production from household food wastes: a review. Bioresour Technol 2018;257:311–9.
[65] Baldi F, Pecorini I, Iannelli R. Comparison of single-stage and two-stage anaerobic co-digestion of food waste and activated sludge for hydrogen and methane production. Renew Energy 2019;143:1755–65.
[66] Nasr N, Elbeshbishy E, Hafez H, Nakhla G, El Naggar MH. Comparative assessment of single-stage and two-stage anaerobic digestion for the treatment of thin stillage. Bioresour Technol 2012;111:122–6.
[67] Schievano A, Tenca A, Scaglia B, Merlino G, Rizzi A, Daffonchio D, et al. Two-stage vs single-stage thermophilic anaerobic digestion: comparison of energy production and biodegradation efficiencies. Environ Sci Technol 2012;46:8502–10.
[68] Zhou M, Yan B, Wong JW, Zhang Y. Enhanced volatile fatty acids production from anaerobic fermentation of food waste: a mini-review focusing on acidogenic metabolic pathways. Bioresour Technol 2018;248:68–78.
[69] Yin J, Yu X, Wang K, Shen D. Acidogenic fermentation of the main substrates of food waste to produce volatile fatty acids. Int J Hydrogen Energy 2016;41:21713–20.
[70] Xiao B, Zhang W, Yi H, Qin Y, Wu J, Liu J, et al. Biogas production by two-stage thermophilic anaerobic co-digestion of food waste and paper waste: effect of paper waste ratio. Renew Energy 2019;132:1301–9.
[71] Sinbuathong N, Sirirote P, Sillapacharoenkul B, Munakata-Marr J, Chulalaksanankul S. Biogas production from two-stage anaerobic digestion of *Jatropha curcas* seed cake. Energy Sources Part A 2012;34:2048–56.
[72] Li W, Loh K-C, Zhang J, Tong YW, Dai Y. Two-stage anaerobic digestion of food waste and horticultural waste in high-solid system. Appl Energy 2018;209:400–8.
[73] Liu CM, Wachemo AC, Yuan HR, Zou DX, Liu YP, Zhang L, et al. Evaluation of methane yield using acidogenic effluent of NaOH pretreated corn stover in anaerobic digestion. Renew Energy 2018;116:224–33.
[74] Srisowmeya G, Chakravarthy M, Devi GN. Critical considerations in two-stage anaerobic digestion of food waste – a review. Renew Sustain Energy Rev 2020;119:109587.
[75] Wang Q, Liang Y, Zhao P, Li QX, Guo S, Chen C. Potential and optimization of two-phase anaerobic digestion of oil refinery waste activated sludge and microbial community study. Sci Rep 2016;6:38245.
[76] Adekunle KF, Okolie JA. A review of biochemical process of anaerobic digestion. Adv Biosci Biotechnol 2015;6:55061.
[77] Olugasa T T, Odesola F, Oyewola MO. Energy production from biogas: a conceptual review for use in Nigeria. Renew Sustain Energy Rev 2014;32:770–6.
[78] Miltner M, Makaruk A, Harasek M. Review on available biogas upgrading technologies and innovations towards advanced solutions. J Clean Prod 2017;161:1329–37.
[79] Leonzio G. Upgrading of biogas to bio-methane with chemical absorption process: simulation and environmental impact. J Clean Prod 2016;131:364–75.
[80] Fradler KR, Kim JR, Shipley G, Massanet-Nicolau J, Dinsdale RM, Guwy AJ, et al. Operation of a bioelectrochemical system as a polishing stage for the effluent from a two-stage biohydrogen and biomethane production process. Biochem Eng J 2014;85:125–31.
[81] Kim T, An J, Jang JK, Chang IS. Coupling of anaerobic digester and microbial fuel cell for COD removal and ammonia recovery. Bioresour Technol 2015;195:217–22.
[82] PepèSciarria T, Tenca A, D'Epifanio A, Mecheri B, Merlino G, Barbato M, et al. Using olive mill wastewater to improve performance in producing electricity from domestic wastewater by using single-chamber microbial fuel cell. Bioresour Technol 2013;147:246–53.
[83] Mohanakrishna G, Mohan VS, Sarma PN. Utilizing acid-rich effluents of fermentative hydrogen production process as substrate for harnessing bioelectricity: an integrative approach. Int J Hydrogen Energy 2010;35:3440–9.
[84] Du Z, Li H, Gu T. A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 2007;25:464–82.
[85] Kadier A, Simayi Y, Kalil MS, Abdeshahian P, Hamid AA. A review of the substrates used in microbial electrolysis cells (MECs) for producing sustainable and clean hydrogen gas. Renew Energy 2014;71:466–72.
[86] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, et al. Microbial fuel cells: methodology and technology. Environ Sci Technol 2006;40:5181–92.
[87] Sharma Y, Li B. Optimizing energy harvest in wastewater treatment by combining anaerobic hydrogen producing biofermentor (HPB) and microbial fuel cell (MFC). Int J Hydrogen Energy 2010;35:3789–97.
[88] Liu H, Cheng S, Logan BE. Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. Environ Sci Technol 2005;39:658–62.
[89] Zhang E, Xu W, Diao G, Shuang C. Electricity generation from acetate and glucose by sedimentary bacterium attached to electrode in microbial-anode fuel cells. J Power Sources 2006;161:820–5.
[90] Kaur R, Marwaha A, Chhabra VA, Kim K-H, Tripathi SK. Recent developments on functional nanomaterial-based electrodes for microbial fuel cells. Renew Sustain Energy Rev 2020;119:109551.
[91] Chiranjeevi P, Patil SA. Strategies for improving the electroactivity and specific metabolic functionality of microorganisms for various microbial electrochemical technologies. Biotechnol Adv 2020;39:107468.
[92] Sekoai PT, Kana EBK. Semi-pilot scale production of hydrogen from Organic Fraction of Solid Municipal Waste and electricity generation from process effluents. Biomass Bioenergy 2014;60:156–63.
[93] Pachapur VL, Sarma SJ, Brar SK, Bihan YL, Soccol CR, Buelna G, et al. Co-culture strategies for increased biohydrogen production. Int J Energy Res 2015;39:1479–504.
[94] Ozgur E, Mars AE, Peksel B, Louwerse A, Yucel M, Gunduz U, et al. Biohydrogen production from beet molasses by sequential dark and photofermentation. Int J Hydrogen Energy;35:511-517.
[95] Escapa A, Mateos R, Martinez EJ, Blanes J. Microbial electrolysis cells: an emerging technology for wastewater treatment and energy recovery. From laboratory to pilot plant and beyond. Renew Sustain Energy Rev 2016;55:942–56.
[96] Hay JXW, Wu TY, Juan JC, Jahim JM. Biohydrogen production through photo fermentation or dark fermentation using waste as a substrate: overview, economics, and future prospects of hydrogen usage. Biofuel Bioprod Biorefin 2013;7:334–52.
[97] Basak N, Jana AK, Das D, Saikia D. Photofermentative molecular biohydrogen production by purple-non-sulfur (PNS) bacteria in various modes: the present progress and future perspective. Int J Hydrogen Energy 2014;39:6853–71.
[98] Barahona E, Jiménez-Vicente E, Rubio LM. Hydrogen overproducing nitrogenases obtained by random mutagenesis and high-throughput screening. Sci Rep 2016;6:38291.
[99] Koku H, Eroglu I, Gunduz U, Yucel M, Turker L. Aspects of the metabolism of hydrogen production by *Rhodobacter* sphaeroides. Int J Hydrogen Energy 2002;27:1315–29.
[100] Kars G, Gunduz U, Yucel M, Turker L, Eroglu I. Hydrogen production and transcriptional analysis of nifD, nifK and hupS genes in *Rhodobacter sphaeroides* O.U.001 grown in media with different concentrations of molybdenum and iron. Int J Hydrogen Energy 2006;31:1536–44.
[101] Uyar B, Schumacher M, Gebicki J, Modigell M. Photoproduction of hydrogen by Rhodobacter capsulatus from thermophilic fermentation effluent. Bioproc Biosyst Eng 2008;32:603606.
[102] Liu B-F, Ren N-Q, Ding J, Xie G-J, Guo W-Q. The effect of Ni^{2+}, Fe^{2+} and Mg^{2+} concentration on photo-hydrogen production by *Rhodopseudomonas faecalis* RLD-53. Int J Hydrogen Energy 2009;34:721–6.
[103] Ren H-Y, Liu B-F, Ding J, Nan J, Xie G-J, Zhao L, et al. Enhanced photo-hydrogen production of *Rhodopseudomonas faecalis* RLD-53 by EDTA addition. Int J Hydrogen Energy 2012;37:8277–81.
[104] Rai PK, Singh SP. Integrated dark- and photo-fermentation: recent advances and provisions for improvement. Int J Hydrogen Energy 2016;41:19957–71.
[105] Lo Y-C, Chen S-D, Chen C-Y, Huang T-I, Lin C-Y, Chang J-S. Combining enzymatic hydrolysis and dark–photo fermentation processes for hydrogen production from starch feedstock: a feasibility study. Int J Hydrogen Energy 2008;33:5224–33.
[106] Noori MT, Ghangrekar MM, Mukherjee CK, Min B. Biofouling effects on the performance of microbial fuel cells and recent advances in biotechnological and chemical strategies for mitigation. Biotechnol Adv 2019;37:107420.
[107] Yasri N, Roberts EPL, Gunasekaran S. The electrochemical perspective of bioelectrocatalytic activities in microbial electrolysis and microbial fuel cells. Energy Rep 2019;5:1116–36.
[108] Yossan S, Xiao L, Prasertsan P, He Z. Hydrogen production in microbial electrolysis cells: choice of catholyte. Int J Hydrogen Energy 2013;38:9619–24.
[109] Kadier A, Simayi Y, Abdeshahian P, Azman NF, Chandrasekhar K, Kalil MS. A comprehensive review of microbial electrolysis cells (MEC) reactor designs and configurations for sustainable hydrogen gas production. Alexandria Eng J 2016;55:427–43.
[110] Wang A, Sun D, Cao G, Wang H, Ren N, Wu W-M, et al. Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell. Bioresour Technol 2011;102:4137–43.
[111] Liu W, Huang S, Zhou A, Zhou G, Ren N, Wang A, et al. Hydrogen generation in microbial electrolysis cell feeding with fermentation liquid of waste activated sludge. Int J Hydrogen Energy 2012;37:13859–64.
[112] San-Martín MI, Sotres A, Alonso RM, Díaz-Marcos J, Morána A, Escapa A. Assessing anodic microbial populations and membrane ageing in a pilot microbial electrolysis cell. Int J Hydrogen Energy 2019;44:17304–15.
[113] Sciarria TP, Arioli S, Gargari G, More D, Adani F. Monitoring microbial communities' dynamics during the start-up of microbial fuel cells by high-throughput screening techniques. Biotechnol Rep 2019;21:e00310.
[114] Lu L, Ren ZJ. Microbial electrolysis cells for waste biorefinery: a state of the art review. Bioresour Technol 2016;215:254–64.
[115] Tuna E, Kargi F, Argun H. Hydrogen gas production by electrohydrolysis of volatile fatty acid (VFA) containing dark fermentation effluent. Int J Hydrogen Energy 2009;34:262–9.
[116] Lee WS, Chua ASM, Yeoh HK, Ngoh GC. A review of the production and applications of waste-derived volatile fatty acids. Chem Eng J 2014;235:83–99.
[117] Vijayaraghavan K, Sagar GK. Anaerobic digestion and in situ electrohydrolysis of dairy bio-sludge. Biotechnol Bioproc Eng 2010;15:520–6.
[118] Vijayaraghavan K, Sagar GK. Anaerobic digestion and in situ electrohydrolysis of dairy bio-sludge. Biotechnol Bioproc Eng 2010;15:520–6.
[119] Taufiq-Yap YH, Teo SH, Rashid U, Islam A, Hussein MZ, Lee KT. Transesterification of *Jatropha curcas* crude oil to biodiesel on calcium lanthanum mixed oxide catalyst: effect of stoichiometric composition. Energy Convers Manag 2014;88:1290–6.

[120] Pollitt KJG, Chhan D, Rais K, Pan K, Wallace JS. Biodiesel fuels: a greener diesel? A review from a health perspective. Sci Total Environ 2019;688:1036–55.
[121] Niju S, Balajii M, Anushya C. A comprehensive review on biodiesel production using Moringa oleifera oil. Int J Green Energy 2018;16:702–15.
[122] Tsoutsos T, Tournaki S, Gkouskos Z, Paraiba O, Giglio F, Garcia PQ, et al. Quality characteristics of biodiesel produced from used cooking oil in southern Europe. Chemengineering 2018;3:19.
[123] Balat M. Potential alternatives to edible oils for biodiesel production – a review of current work. Energy Convers Manag 2011;52:1479–92.
[124] Muscat A, de Olde EM, Bde Boer IJM, Ripoll-Bosch R. The battle for biomass: a systematic review of food-feed-fuel competition. Global Food Security 2019; 100330. https://doi.org/10.1016/j.gfs.2019.100330.
[125] Tenenbaum DJ. Food vs. Fuel: diversion of crops could cause more hunger. Environ Health Perspect 2008;116:A254–7.
[126] Oumer AN, Hasan MM, Baheta AT, Mamat R, Abdullah AA. Bio-based liquid fuels as a source of renewable energy: a review. Renew Sustain Energy Rev 2018;88: 82–98.
[127] Nayak A, Bhushan B. An overview of the recent trends on the waste valorization techniques for food wastes. J Environ Manag 2019;233:352–70.
[128] Park GW, Chang HN, Jung K, Seo C, Kim Y-C, Choi JH, et al. Production of microbial lipid by *Cryptococcus curvatus* on rice straw hydrolysates. Process Biochem 2017;56:147–53.
[129] Liu J, Yuan M, Liu J-N, Huang X-F. Bioconversion of mixed volatile fatty acids into microbial lipids by cryptococcus curvatus ATCC 20509. Bioresour Technol 2017;241:645–51.
[130] Fei Q, Chang HH, Shang L, Choi J-d-r, Kim N, Kang J. The effect of volatile fatty acids as a sole carbon source on lipid accumulation by *Cryptococcus albidus* for biodiesel production. Bioresour Technol 2011;102:2695–701.
[131] Kurniawan A, Kwon SY, Shin J-H, Hur J, Cho J. Acid fermentation process combined with post denitrification for the treatment of primary sludge and wastewater with high strength nitrate. Water 2016;8:117.
[132] He X, Wareham DG. The use of naturally generated volatile fatty acids for herbicide removal via denitrification. J Environ Sci Health B 2009;44:302–10.
[133] Lappa K, Kandylis P, Bastas N, Klaoudatos S, Athanasopoulos N, Bekatorou A, et al. New generation biofuel: continuous acidogenesis of sucrose–raffinose mixture simulating vinasse is promoted by calumina pellets. Biotechnol Fuels 2015;8:74.
[134] Chen W-H, Jian Z-C. Evaluation of recycling the effluent of hydrogen fermentation for biobutanol production: kinetic study with butyrate and sucrose concentrations. Chemosphere 2013;93:597–603.
[135] Chen W, Chen S, Chao S, Jian Z. Butanol production from the effluent of hydrogen fermentation. Water Sci Technol 2011;63:1236–40.
[136] Mohan SV. Harnessing of biohydrogen from wastewater treatment using mixed fermentative consortia: process evaluation towards optimization. Int J Hydrogen Energy 2009;34:7460–74.
[137] Kapdan IK, Kargi F. Bio-hydrogen production from waste materials. Enzym Microb Technol 2006;38:569–82.
[138] Farouk RY, Li L, Wang Y, Li Y, Melak S. Influence of pretreatment and pH on the enhancement of hydrogen and volatile fatty acids production from food waste in the semi-continuously running reactor. Int J Hydrogen Energy 2020;45:3729–38.
[139] Zhang B, Zhang L, Zhang S, Shi H, Cai W. The influence of pH on hydrolysis and acidogenesis of kitchen wastes in two-phase anaerobic digestion. Environ Technol 2005;26:329–40.
[140] Lay C-H, Sung I-Y, Kumar G, Chu C-Y, Chen C-C, Lin C-Y. Optimizing biohydrogen production from mushroom cultivation waste using anaerobic mixed cultures. Int J Hydrogen Energy 2012;37:16473–8.
[141] Choi J, Ahn Y. Biohydrogen fermentation from sucrose and piggery waste with high levels of bicarbonate alkalinity. Energies 2015;8:1716–29.
[142] Xiao N, Chen Y, Chen A, Feng L. Enhanced bio-hydrogen production from protein wastewater by altering protein structure and amino acids acidification type. Sci Rep 2014;4:3992.
[143] Lee YJ, Miyahara T, Noike T. Effect of pH on microbial hydrogen fermentation. J Chem Technol Biotechnol 2002;77:694–8.
[144] Faloye F, Kana EG, Schmidt S. Optimization of biohydrogen inoculum development via a hybrid pH and microwave treatment technique–Semi pilot scale production assessment. Int J Hydrogen Energy 2014;39:5607–16.
[145] Kim M-S, Kim D-H, Yun Y-M. Effect of operation temperature on anaerobic digestion of food waste: performance and microbial analysis. Fuel 2017;209: 598–605.
[146] Kim JK, Oh BR, Chun YN, Kim SW. Effects of temperature and hydraulic retention time on anaerobic digestion of food waste. J Biosci Bioeng 2006;102:328–32.
[147] Mamimin C, Prasertsan P, Kongjan P, Sompong O. Effects of volatile fatty acids in biohydrogen effluent on biohythane production from palm oil mill effluent under thermophilic condition. Electron J Biotechnol 2017;29:78–85.
[148] Hao J, Wang H. Volatile fatty acids productions by mesophilic and thermophilic sludge fermentation: biological responses to fermentation temperature. Bioresour Technol 2015;175:367–73.
[149] Liu H, Han P, Liu H, Zhou G, Fu B, Zheng Z. Full-scale production of VFAs from sewage sludge by anaerobic alkaline fermentation to improve biological nutrients removal in domestic wastewater. Bioresour Technol 2018;260:105–14.
[150] Zhang P, Chen Y, Zhou Q. Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: effect of pH. Water Res 2009;43:3735–42.
[151] Wilson CA, Murthy S, Fang Y, Novak J. The effect of temperature on the performance and stability of thermophilic anaerobic digestion. Water Sci Technol 2008;57:297–304.
[152] Ma H, Liu H, Zhang L, Yang M, Fu B, Liu H. Novel insight into the relationship between organic substrate composition and volatile fatty acids distribution in acidogenic co-fermentation. Biotechnol Biofuels 2017;10:137.
[153] Zhang C, Su H, Baeyens J, Tan T. Reviewing the anaerobic digestion of food waste for biogas production. Renew Sustain Energy Rev 2014;38:383–92.
[154] Luli GW, Strohl WR. Comparison of growth, acetate production, and acetate inhibition of Escherichia coli strains in batch and fed-batch fermentations. Appl Environ Microbiol 1990;56:1004–11.
[155] Sekoai PT, Awosusi AA, Yoro KO, Singo M, Oloye O, Ayeni AO, et al. Microbial cell immobilization in biohydrogen production: a short overview. Crit Rev Biotechnol 2018;38:157–71.
[156] Chohan NA, Aruwajoye G, Sewsynker-Sukai Y, Kana EG. Valorisation of potato peel wastes for bioethanol production using simultaneous saccharification and fermentation: process optimization and kinetic assessment. Renew Energy 2020; 146:1031–40.
[157] Moodley P, Kana EG. Development of a steam or microwave-assisted sequential salt-alkali pretreatment for lignocellulosic waste: effect on delignification and enzymatic hydrolysis. Energy Convers Manag 2017;148:801–8.
[158] Ariunbaatar J, Panico A, Esposito G, Pirozzi F, Lens PN. Pretreatment methods to enhance anaerobic digestion of organic solid waste. Appl Energy 2014;123: 143–56.
[159] Cheah Y-K, Dosta J, Mata-Álvarez J. Enhancement of volatile fatty acids production from food waste by mature compost addition. Molecules 2019;24: 2986.
[160] Jayakrishnan U, Deka D, Das G. Enhancing the volatile fatty acid production from agro-industrial waste streams through sludge pretreatment. Environ Sci: Water Res Technol 2019;5:334–45.
[161] Jin D, Chen J, Lun S. Production of poly (hydroxyalkanoate) by a composite anaerobic acidification–fermentation system. Process Biochem 1999;34:829–33.
[162] Silva FC, Serafim LS, Nadais H, Arroja L, Capela I. Acidogenic fermentation towards valorisation of organic waste streams into volatile fatty acids. Chem Biochem Eng Q 2013;27:467–76.
[163] Ucisik AS, Henze M. Biological hydrolysis and acidification of sludge under anaerobic conditions: the effect of sludge type and origin on the production and composition of volatile fatty acids. Water Res 2008;42:3729–38.
[164] Rabii A, Aldin S, Dahman Y, Elbeshbishy E. A review on anaerobic co-digestion with a focus on the microbial populations and the effect of multi-stage digester configuration. Energies 2019;12:1106.
[165] Mata-Alvarez J, Dosta J, Romero-Güiza M, Fonoll X, Peces M, Astals S. A critical review on anaerobic co-digestion achievements between 2010 and 2013. Renew Sustain Energy Rev 2014;36:412–27.
[166] Lomborg CJ, Holm-Nielsen JB, Oleskowicz-Popiel P, Esbensen KH. Near infrared and acoustic chemometrics monitoring of volatile fatty acids and dry matter during co-digestion of manure and maize silage. Bioresour Technol 2009;100: 1711–9.
[167] Cheah Y-K, Vidal-Antich C, Dosta J, Mata-Álvarez J. Volatile fatty acid production from mesophilic acidogenic fermentation of organic fraction of municipal solid waste and food waste under acidic and alkaline pH. Environ Sci Pollut Res 2019; 26:35509–22.
[168] Chandrasekhar K, Lee YJ, Lee DW. Biohydrogen production: strategies to improve process efficiency through microbial routes. Int J Mol Sci 2015;16:8266–93.
[169] Kim HM, Park JH, Choi IS, Wi SG, Ha S, Chun HH, et al. Effective approach to organic acid production from agricultural kimchi cabbage waste and its potential application. PloS One 2018;13.
[170] Dong L, Zhenhong Y, Yongming S, Xiaoying K, Yu Z. Hydrogen production characteristics of the organic fraction of municipal solid wastes by anaerobic mixed culture fermentation. Int J Hydrogen Energy 2009;34:812–20.
[171] Taheri E, Amin MM, Pourzamani H, Fatehizadeh A, Ghasemian M, Bina B. Comparison of acetate-butyrate and acetate-ethanol metabolic pathway in biohydrogen production. J Med Signals Sens 2018;8:101–7.
[172] Alibardi L, Cossu R. Effects of carbohydrate, protein and lipid content of organic waste on hydrogen production and fermentation products. Waste Manag 2016;47: 69–77.
[173] Oh ST, Martin AD. Long chain fatty acids degradation in anaerobic digester: thermodynamic equilibrium consideration. Process Biochem 2010;45:335–45.
[174] Battista F, Bolzonella D. Some critical aspects of the enzymatic hydrolysis at high dry matter content: a review. Biofuel Bioprod Biorefin 2018;12:711–23.
[175] Shen D, Yin J, Yu X, Wang M, Long Y, Shentu J, et al. Acidogenic fermentation characteristics of different types of protein-rich substrates in food waste to volatile fatty acids. Bioresour Technol 2017;227:125–32.
[176] Rehan M, Nizami A-S, Rashid U, Naqvi RM. Editorial: waste biorefineries: future energy, green products and waste treatment. Front Energy Res 2019;7:55.
[177] Wang K, Yin J, Shen DS, Li N. Anaerobic digestion of food waste for volatile fatty acids (VFAs) production with different types of inoculums: effect of pH. Bioresour Technol 2014;161:395–401.
[178] Chen H, Wu HY. Optimization of volatile fatty acid production with co-substrate of food wastes and dewatered excess sludge using response surface methodology. Bioresour Technol 2010;101:5487–93.
[179] Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PN, et al. A review on dark fermentative biohydrogen production from organic biomass: process parameters and use of by-products. Appl Energy 2015;144:73–95.
[180] Sekoai PT, Mhlongo SI, Ezeokoli OT. Progress in the development of methods used for the abatement of microbial contaminants in ethanol fermentations: a review. Rev Environ Sci Biotechnol 2019;18:795–821.
[181] Zupancic J, Raghupathi PK, Houf K, Burmolle M, Sorensen SJ, Gunde-Cimerman N. Synergistic interactions in microbial biofilms facilitate the

establishment of opportunistic pathogenic fungi in household dishwashers. Front Microbiol 2018;9:21.
[182] Deng Y-J, Wang SY. Synergistic growth in bacteria depends on substrate complexity. J Microbiol 2016;54:23–30.
[183] Lecker B, Illi L, Lemmer A, Oechsner H. Biological hydrogen methanation–a review. Bioresour Technol 2017;245:1220–8.
[184] Agneessens LM, Ottosen LDM, Andersen M, Olesen CB, Feilberg A, Kofoed MVW. Parameters affecting acetate concentrations during in-situ biological hydrogen methanation. Bioresour Technol 2018;258:33–40.
[185] Luo G, Johansson S, Boe K, Xie L, Zhou Q, Angelidaki I. Simultaneous hydrogen utilization *in situ* biogas upgrading. Biotechnol Bioeng 2012;109:1089–94.
[186] Kougias PG, Treu L, Benavente DP, Boe K, Campanaro S, Angelidaki I. Ex-situ biogas upgrading and enhancement in different reactor systems. Bioresour Technol 2017;225:429–37.
[187] Carrere H, Antonopoulou G, Affes R, Passos F, Battimelli A, Lyberatos G, et al. Review of feedstock pretreatment strategies for improved anaerobic digestion: from lab-scale research to full-scale application. Bioresour Technol 2016;199:386–97.
[188] Fang HHP, Liu H. Effect of pH hydrogen production from glucose by a mixed culture. Bioresour Technol 2002;82:87–93.
[189] Yuan HY, Chen YG, Zhang HX, Jiang S, Zhou Q, Gu GW. Improved bioproduction of short-chain fatty acids (SCFAs) from excess sludge under alkaline conditions. Environ Sci Technol 2006;40:2025–9.
[190] Boe K, Angelidaki I. Pilot-scale application of an online VFA sensor for monitoring and control of a manure digester. Water Sci Technol 2012;66:2496–503.
[191] Freguia S, Teh EH, Boon N, Leung KM, Keller J, Rabaey K. Microbial fuel cells operating on mixed fatty acids. Bioresour Technol 2010;101:1233–8.
[192] Bengtsson S, Hallquist J, Werker A, Welander T. Acidogenic fermentation of industrial wastewaters: effects of chemostat retention time and pH on volatile fatty acids production. Biochem Eng J 2008;40:492–9.
[193] Eggeman T, Verser D. Recovery of organic acids from fermentation broths. In: Davison BH, Evans BR, Finkelstein M, McMillan JD, editors. Twenty-sixth symposium on biotechnology for fuels and chemicals. Humana Press; 2005. p. 605–18.
[194] Schlosser Š, Kertész R, Marták J. Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: an overview with a case study on recovery of MPCA. Separ Purif Technol 2005;41:237–66.
[195] Jankowska E, Duber A, Chwialkowska J, Stodolny M, Oleskowicz-Popiel P. Conversion of organic waste into volatile fatty acids–The influence of process operating parameters. Chem Eng J 2018;345:395–403.
[196] Wong LP, Isa MH, Bashir MJ, Chin YH. Effect of hydraulic retention time on volatile fatty acid production and organic degradation in anaerobic digestion of palm oil mill effluent. In: AIP conference proceedings. AIP Publishing LLC; 2019, 020020.
[197] Jankowska E, Chwialkowska J, Stodolny M, Oleskowicz-Popiel P. Effect of pH and retention time on volatile fatty acids production during mixed culture fermentation. Bioresour Technol 2015;190:274–80.
[198] Wainaina S, Lukitawesa, Kumar Awasthi M, Taherzadeh MJ. Bioengineering of anaerobic digestion for volatile fatty acids, hydrogen or methane production: a critical review. Bioengineered 2019;10:437–58.
[199] Yuan Y, Hu X, Chen H, Zhou Y, Zhou Y, Wang D. Advances in enhanced volatile fatty acid production from anaerobic fermentation of waste activated sludge. Sci Total Environ 2019:133741.
[200] Lim S-J, Kim BJ, Jeong C-M, Choi J-d-r, Ahn YH, Chang HN. Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor. Bioresour Technol 2008;99:7866–74.
[201] Banerjee A, Elefsiniotis P, Tuhtar D. Effect of HRT and temperature on the acidogenesis of municipal primary sludge and industrial wastewater. Water Sci Technol 1998;38:417–23.
[202] Chen Y, Zhang F, Wang T, Shen N, Yu Z-W, Zeng RJ. Hydraulic retention time affects stable acetate production from tofu processing wastewater in extreme-thermophilic (70 C) mixed culture fermentation. Bioresour Technol 2016;216:722–8.
[203] Li L, Wang Y, Li Y. Effects of substrate concentration, hydraulic retention time and headspace pressure on acid production of protein by anaerobic fermentation. Bioresour Technol 2019;283:106–11.
[204] Zhang Z-P, Show K-Y, Tay J-H, Liang DT, Lee D-J, Jiang W-J. Effect of hydraulic retention time on biohydrogen production and anaerobic microbial community. Process Biochem 2006;41:2118–23.
[205] Uyar B, Eroglu I, Yücel M, Gündüz U. Photofermentative hydrogen production from volatile fatty acids present in dark fermentation effluents. Int J Hydrogen Energy 2009;34:4517–23.
[206] Yun J, Cho KS. Effects of organic loading rate on hydrogen and volatile fatty acid production and microbial community during acidogenic hydrogenesis in a continuous stirred tank reactor using molasses wastewater. J Appl Microbiol 2016;121:1627–36.
[207] Wijekoon KC, Visvanathan C, Abeynayaka A. Effect of organic loading rate on VFA production, organic matter removal and microbial activity of a two-stage thermophilic anaerobic membrane bioreactor. Bioresour Technol 2011;102:5353–60.
[208] Khan MA, Ngo HH, Guo W, Liu Y, Nghiem LD, Chang SW, et al. Optimization of hydraulic retention time and organic loading rate for volatile fatty acid production from low strength wastewater in an anaerobic membrane bioreactor. Bioresour Technol 2019;271:100–8.
[209] Rincón B, Borja R, González J, Portillo M, Sáiz-Jiménez C. Influence of organic loading rate and hydraulic retention time on the performance, stability and microbial communities of one-stage anaerobic digestion of two-phase olive mill solid residue. Biochem Eng J 2008;40:253–61.
[210] Sekoai PT, Yoro KO, Daramola MO. Effect of nitrogen gas sparging on dark fermentative biohydrogen production using suspended and immobilized cells of anaerobic mixed bacteria from potato waste. Biofuels 2018;9:595–604.
[211] Khanal SK, Chen W-H, Li L, Sung S. Biological hydrogen production: effects of pH and intermediate products. Int J Hydrogen Energy 2004;29:1123–31.
[212] Chong M-L, Sabaratnam V, Shirai Y, Hassan MA. Biohydrogen production from biomass and industrial wastes by dark fermentation. Int J Hydrogen Energy 2009;34:3277–87.
[213] Levin DB, Pitt L, Love M. Biohydrogen production: prospects and limitations to practical application. Int J Hydrogen Energy 2004;29:173–85.
[214] Mandal B, Nath K, Das D. Improvement of biohydrogen production under decreased partial pressure of H 2 by Enterobacter cloacae. Biotechnol Lett 2006;28:831–5.
[215] Oh S-E, Zuo Y, Zhang H, Guiltinan MJ, Logan BE, Regan JM. Hydrogen production by *Clostridium acetobutylicum* ATCC 824 and megaplasmid-deficient mutant M5 evaluated using a large headspace volume technique. Int J Hydrogen Energy 2009;34:9347–53.
[216] Zhou M, Zhou J, Tan M, Du J, Yan B, Wong JW, et al. Enhanced carboxylic acids production by decreasing hydrogen partial pressure during acidogenic fermentation of glucose. Bioresour Technol 2017;245:44–51.
[217] Nguyen TAD, Han SJ, Kim JP, Kim MS, Sim SJ. Hydrogen production of the hyperthermophilic eubacterium, *Thermotoga neapolitana* under N2 sparging condition. Bioresour Technol 2010;101:S38–41.
[218] Kim DH, Han SK, Kim SH. Effect of gas sparging on continuous fermentative hydrogen production. Int J Hydrogen Energy 2006;31:2158–69.
[219] Mizuno O, Dinsdale R, Hawkes FR. Enhancement of hydrogen production from glucose by nitrogen gas sparging. Bioresour Technol 2000;73:56–65.
[220] Mateos R, Sotres A, Alonso RM, Morán A, Escapa A. Enhanced CO_2 conversion to acetate through microbial electrosynthesis (MES) by continuous headspace gas recirculation. Energies 2019;12:3297.
[221] Zhang F, Chen Y, Dai K, Shen N, Zeng RJ. The glucose metabolic distribution in thermophilic (55 C) mixed culture fermentation: a chemostat study. Int J Hydrogen Energy 2015;40:919–26.
[222] Aslam M, Ahmad R, Yasin M, Khan AL, Shahid MK, Hossain S, et al. Anaerobic membrane bioreactors for biohydrogen production: recent developments, challenges and perspectives. Bioresour Technol 2018;269:452–64.
[223] Rittmann S, Herwig C. A comprehensive and quantitative review of dark fermentative biohydrogen production. Microb Cell Factories 2012;11:115.
[224] Karthikeyan OP, Selvam A, Wong JW. Hydrolysis–acidogenesis of food waste in solid–liquid-separating continuous stirred tank reactor (SLS-CSTR) for volatile organic acid production. Bioresour Technol 2016;200:366–73.
[225] Lin CY, Chang RC. Hydrogen production during the anaerobic acidogenic conversion of glucose. J Chem Technol Biotechnol 1999;74:498–500.
[226] Ri P-C, Kim J-S, Kim T-R, Pang C-H, Mun H-G, Pak G-C, et al. Effect of hydraulic retention time on the hydrogen production in a horizontal and vertical continuous stirred-tank reactor. Int J Hydrogen Energy 2019;44:17742–9.
[227] Chang S, Li J, Liu F. Continuous biohydrogen production from diluted molasses in an anaerobic contact reactor. Front Environ Sci Eng China 2011;5:140–8.
[228] Kongjan P, Angelidaki I. Extreme thermophilic biohydrogen production from wheat straw hydrolysate using mixed culture fermentation: effect of reactor configuration. Bioresour Technol 2010;101:7789–96.
[229] Trad Z, Vial C, Fontaine J-P, Larroche C. Modeling of hydrodynamics and mixing in a submerged membrane bioreactor. Chem Eng J 2015;282:77–90.
[230] Khan MA, Ngo HH, Guo W, Chang SW, Nguyen DD, Varjani S, et al. Selective production of volatile fatty acids at different pH in an anaerobic membrane bioreactor. Bioresour Technol 2019;283:120–8.
[231] Lim JX, Vadivelu VM. E. nhanced volatile fatty acid production in sequencing batch reactor: microbial population and growth kinetics evaluation. AIP Conference Proceedings: AIP Publishing LLC; 2019, 020040.
[232] Tamis J, Joosse B, Mv Loosdrecht, Kleerebezem R. High-rate volatile fatty acid (VFA) production by a granular sludge process at low pH. Biotechnol Bioeng 2015;112:2248–55.
[233] Amani T, Nosrati M, Mousavi SM, Kermanshahi RK. Analysis of the syntrophic anaerobic digestion of volatile fatty acids using enriched cultures in a fixed-bed reactor. Water Environ Res 2012;84:460–72.
[234] Sivagurunathan P, Anburajan P, Park J-H, Kumar G, Park H-D, Kim S-H. Mesophilic biogenic H_2 production using galactose in a fixed bed reactor. Int J Hydrogen Energy 2017;42:3658–66.
[235] Amorim N, Alves I, Martins J, Amorim E. Biohydrogen production from cassava wastewater in an anaerobic fluidized bed reactor. Braz J Chem Eng 2014;31:603–12.
[236] Celis-García LB, Razo-Flores E, Monroy O. Performance of a down-flow fluidized bed reactor under sulfate reduction conditions using volatile fatty acids as electron donors. Biotechnol Bioeng 2007;97:771–9.
[237] Dohanyos M, Kosova B, Zabranska J, Grau P. Production and utilization of volatile fatty acids in various types of anaerobic reactors. Water Sci Technol;17:191-205.
[238] Wong B-T, Show K-Y, Su A, Wong R-j, Lee D-J. Effect of volatile fatty acid composition on upflow anaerobic sludge blanket (UASB) performance. Energy Fuel 2008;22:108–12.
[239] Weide T, Brügging E, Wetter C, Ierardi A, Wichern M. Use of organic waste for biohydrogen production and volatile fatty acids via dark fermentation and further processing to methane. Int J Hydrogen Energy 2019;44:24110–25.

[240] Slezak R, Grzelak J, Krzystek L, Ledakowicz S. The effect of initial organic load of the kitchen waste on the production of VFA and H2 in dark fermentation. Waste Manag 2017;68:610–7.
[241] Grzelak J, Ślęzak R, Krzystek L, Ledakowicz S. Effect of pH on the production of volatile fatty acids in dark fermentation process of organic waste. Ecol Chem Eng S 2018;25:295–306.
[242] Islam MS, Guo C, Liu C-Z. Enhanced hydrogen and volatile fatty acid production from sweet sorghum stalks by two-steps dark fermentation with dilute acid treatment in between. Int J Hydrogen Energy 2018;43:659–66.
[243] Trevisan V, Monteggia LO, dos Santos Delabary H. A short-term test for the evaluation of hydrogen and volatile fatty acids production from industrial effluents: the use of a short-term test to evaluate organic matter concentration from industrial effluents for the production of hydrogen and volatile fatty acids. Int J Hydrogen Energy 2014;39:7730–4.
[244] Jia X, Li M, Zhu J, Jiang Y, Wang Y, Wang Y. Enhancement split-phase hydrogen production from food waste during dark fermentation: protein substances degradation and transformation during hydrothermal pre-treatments. Int J Hydrogen Energy 2019;44:17334–45.
[245] Infantes D, Del Campo AG, Villaseñor J, Fernández F. Influence of pH, temperature and volatile fatty acids on hydrogen production by acidogenic fermentation. Int J Hydrogen Energy 2011;36:15595–601.
[246] Khanal SK, Chen WH, Li L, Sung S. Biohydrogen production in continuous-flow reactor using mixed microbial culture. Water Environ Res 2006;78:110–7.
[247] Han W, Yan Y, Shi Y, Gu J, Tang J, Zhao H. Biohydrogen production from enzymatic hydrolysis of food waste in batch and continuous systems. Sci Rep 2016;6:38395.
[248] Arooj MF, Han S-K, Kim S-H, Kim D-H, Shin H-S. Continuous biohydrogen production in a CSTR using starch as a substrate. Int J Hydrogen Energy 2008;33:3289–94.
[249] Si B-C, Li J-M, Zhu Z-B, Zhang Y-H, Lu J-W, Shen R-X, et al. Continuous production of biohythane from hydrothermal liquefied cornstalk biomass via two-stage high-rate anaerobic reactors. Biotechnol Biofuels 2016;9:254.
[250] Liu N, Jiang J, Yan F, Xu Y, Yang M, Gao Y, et al. Optimization of simultaneous production of volatile fatty acids and bio-hydrogen from food waste using response surface methodology. RSC Adv 2018;8:10457–64.
[251] Zhao X-x, Fan X-l, Xue Z-x, Yang Z-m, Yuan X-z, Qiu Y-l, et al. Simultaneous production of hydrogen and volatile fatty acids from anaerobic digestion of Macrocystis pyrifera biomass residues. J Cent South Univ 2017;24:1281–7.
[252] Usmanbaha N, Jariyaboon R, Reungsang A, Kongjan P, Chu C-Y. Optimization of batch dark fermentation of *Chlorella* sp. using mixed-cultures for simultaneous hydrogen and butyric acid production. Energies 2019;12:2529.
[253] Rosa PRF, Santos SC, Silva EL. Different ratios of carbon sources in the fermentation of cheese whey and glucose as substrates for hydrogen and ethanol production in continuous reactors. Int J Hydrogen Energy 2014;39:1288–96.
[254] Carrillo-Reyes J, Celis LB, Alatriste-Mondragón F, Razo-Flores E. Decreasing methane production in hydrogenogenic UASB reactors fed with cheese whey. Biomass Bioenergy 2014;63:101–8.
[255] dos Reis CM, Carosia MF, Sakamoto IK, Varesche MBA, Silva EL. Evaluation of hydrogen and methane production from sugarcane vinasse in an anaerobic fluidized bed reactor. Int J Hydrogen Energy 2015;40:8498–509.
[256] Reungsang A, Sittijunda S, Sompong O. Bio-hydrogen production from glycerol by immobilized Enterobacter aerogenes ATCC 13048 on heat-treated UASB granules as affected by organic loading rate. Int J Hydrogen Energy 2013;38:6970–9.
[257] Nguyen M-LT, Hung P-C, Vo T-P, Lay C-H, Lin C-Y. Effect of food to microorganisms (F/M) ratio on biohythane production via single-stage dark fermentation. Int J Hydrogen Energy 2020;46:11313–24.
[258] Sekoai P, Kana EG. A two-stage modelling and optimization of biohydrogen production from a mixture of agro-municipal waste. Int J Hydrogen Energy 2013;38:8657–63.
[259] Ramos LR, Silva EL. Continuous hydrogen production from cofermentation of sugarcane vinasse and cheese whey in a thermophilic anaerobic fluidized bed reactor. Int J Hydrogen Energy 2018;43:13081–9.
[260] Rodríguez-Valderrama S, Escamilla-Alvarado C, Magnin J-P, Rivas-García P, Valdez-Vazquez I, Ríos-Leal E. Batch biohydrogen production from dilute acid hydrolyzates of fruits-and-vegetables wastes and corn stover as co-substrates. Biomass Bioenergy 2020;140:105666.
[261] Robledo-Narváez PN, Muñoz-Páez KM, Poggi-Varaldo HM, Ríos-Leal E, Calva-Calva G, Ortega-Clemente LA, et al. The influence of total solids content and initial pH on batch biohydrogen production by solid substrate fermentation of agroindustrial wastes. J Environ Manag 2013;128:126–37.
[262] Kumari S, Das D. Biohythane production from sugarcane bagasse and water hyacinth: a way towards promising green energy production. J Clean Prod 2019;207:689–701.
[263] Pinto MPM, Mudhoo A, de Alencar Neves T, Berni MD, Forster-Carneiro T. Co–digestion of coffee residues and sugarcane vinasse for biohythane generation. J Environ Chem Eng 2018;6:146–55.
[264] Sekoai PT, Ouma CNM, Du Preez SP, Modisha P, Engelbrecht N, Bessarabov DG, et al. Application of nanoparticles in biofuels: an overview. Fuel 2019;237:380–97.
[265] Pugazhendhi A, Shobana S, Nguyen DD, Banu JR, Sivagurunathan P, Chang SW, et al. Application of nanotechnology (nanoparticles) in dark fermentative hydrogen production. Int J Hydrogen Energy 2019;44:1431–40.
[266] Ganzoury MA, Allam NK. Impact of nanotechnology on biogas production: a mini-review. Renew Sustain Energy Rev 2015;50:1392–404.
[267] Ramprakash B, Incharoensakdi A. Light-driven biological hydrogen production by Escherichia coli mediated by TiO2 nanoparticles. Int J Hydrogen Energy 2020;45:6254–61.
[268] Banu JR, Kavitha S, Kannah RY, Bhosale RR, Kumar G. Industrial wastewater to biohydrogen: possibilities towards successful biorefinery route. Bioresour Technol 2020:122378.
[269] Yang G, Wang J. Improving mechanisms of biohydrogen production from grass using zero-valent iron nanoparticles. Bioresour Technol 2018;266:413–20.
[270] Serrano E, Rus G, Garcia-Martinez J. Nanotechnology for sustainable energy. Renew Sustain Energy Rev 2009;13:2373–84.
[271] Wei W, Cai Z, Fu J, Xie G-J, Li A, Zhou X, et al. Zero valent iron enhances methane production from primary sludge in anaerobic digestion. Chem Eng J 2018;351:1159–65.
[272] Raychoudhury T, Scheytt T. Potential of zerovalent iron nanoparticles for remediation of environmental organic contaminants in water: a review. Water Sci Technol 2013;68:1425–39.
[273] Fahmy HM, Mohamed FM, Marzouq MH, Mustafa ABE-D, Alsoudi AM, Ali OA, et al. Review of green methods of iron nanoparticles synthesis and applications. Bionanoscience 2018;8:491–503.
[274] Blanchette C, Lacayo CI, Fischer NO, Hwang M, Thelen MP. Enhanced cellulose degradation using cellulase-nanosphere complexes. PloS One 2012;7.
[275] Zhao W, Zhang Y, Du B, Wei D, Wei Q, Zhao Y. Enhancement effect of silver nanoparticles on fermentative biohydrogen production using mixed bacteria. Bioresour Technol 2013;142:240–5.
[276] Zhao W, Zhao J, Chen GD, Feng R, Yang J, Zhao YF, et al. Anaerobic biohydrogen production by the mixed culture with mesoporous Fe_3O_4 nanoparticles activation. In: Liu S, Zuo M, editors. Adv Mat Res. Stafa-Zurich. Switzerland: Trans Tech Publications; 2011. p. 1528–31.
[277] Elreedy A, Ibrahim E, Hassan N, El-Dissouky A, Fujii M, Yoshimura C, et al. Nickel-graphene nanocomposite as a novel supplement for enhancement of biohydrogen production from industrial wastewater containing mono-ethylene glycol. Energy Convers Manag 2017;140:133–44.
[278] Dehhaghi M, Tabatabaei M, Aghbashlo M, Panahi HKS, Nizami A-S. A state-of-the-art review on the application of nanomaterials for enhancing biogas production. J Environ Manag 2019;251:109597.
[279] Ali HKQ, Daud MZM, Al-azzawi Z. Economic benefit from the optimization of citric acid production from rice straw through Plackett-Burman design and central composite design. Turk J Eng Environ Sci 2012;36:81–93.
[280] Bari MN, Alam MZ, Muyibi SA, Jamal P. Improvement of production of citric acid from oil palm empty fruit bunches: optimization of media by statistical experimental designs. Bioresour Technol 2009;100:3113–20.
[281] Roukas T, Kotzekidou P. Pomegranate peel waste: a new substrate for citric acid production by Aspergillus Niger in solid-state fermentation under non-aseptic conditions. Environ Sci Pollut Res 2020;27:13105–13.
[282] Show PL, Oladele KO, Siew QY, Aziz Zakry FA, Lan JC-W, Ling TC. Overview of citric acid production from *Aspergillus niger*. Front Life Sci 2015;8:271–83.
[283] Morgunov IG, Kamzolova SV, Lunina JN. Citric acid production by *Yarrowia lipolytica* yeast on different renewable raw materials. Fermentatio 2018;4:36.
[284] Kana EBG, Olokeb JK, Lateefb A, Oyebanjib A. Comparative evaluation of artificial neural network coupled genetic algorithm and response surface methodology for modeling and optimization of citric acid production by *Aspergillus niger* MCBN297. Chem Eng 2012;27:397–402.
[285] Moeller L, Bauer A, Zehnsdorf A, Lee MY, Müller RA. Anaerobic co-digestion of waste yeast biomass from citric acid production and waste frying fat. Eng Life Sci 2018;18:425–33.
[286] Yang H, Shao P, Lu T, Shen J, Wang D, Xu Z, et al. Continuous bio-hydrogen production from citric acid wastewater via facultative anaerobic bacteria. Int J Hydrogen Energy 2006;31:1306–13.
[287] Zhou Q, Zhang G, Lu Y, Wu P. Feasibility study and process optimization of citric acid wastewater treatment and biomass production by photosynthetic bacteria. Desalination Water Treat 2016;57:6261–7.
[288] Rymowicz W, Rywińska A, Gładkowski W. Simultaneous production of citric acid and erythritol from crude glycerol by *Yarrowia lipolytica Wratislavia* K1. Chem Pap 2008;62:239.
[289] Zhang AY-z, Sun Z, Leung CCJ, Han W, Lau KY, Li M, et al. Valorisation of bakery waste for succinic acid production. Green Chem 2013;15:690–5.
[290] Leung CCJ, Cheung ASY, Zhang AY-Z, Lam KF, Lin CSK. Utilisation of waste bread for fermentative succinic acid production. Biochem Eng J 2012;65:10–5.
[291] Industry Analytical Research Consulting. Succinic acid market - forecast. 2020 - 2025. March 22 2020, https://www.industryarc.com/Report/17679/succinic-acid-market.html.
[292] Yang Q, Wu M, Dai Z, Xin F, Zhou J, Dong W, et al. Comprehensive investigation of succinic acid production by *Actinobacillus succinogenes*: a promising native succinic acid producer. Biofuel Bioprod Biorefin 2019;14:950–64. https://doi.org/10.1002/bbb.2058.
[293] Mazière A, Prinsen P, García A, Luque R, Len C. A review of progress in (bio) catalytic routes from/to renewable succinic acid. Biofuel Bioprod Biorefin 2017;11:908–31.
[294] Hanipa MAF, AP M, Jahim JM, Takriff MS, Reungsang A. Valorising fermentation effluent rich in short-chain fatty acids and sugars for biohydrogen via photofermentation by *Rhodobacter sphaeroides* KKU-PS1. IOP Conf Ser Earth Environ Sci 2019;268. https://doi.org/10.1088/1755-1315/268/1/012077.
[295] Babaei M, Tsapekos P, Alvarado-Morales M, Hosseini M, Ebrahimi S, Niaei A, et al. Valorization of organic waste with simultaneous biogas upgrading for the production of succinic acid. Biochem Eng J 2019;147:136–45.

[296] Kuglarz M, Alvarado-Morales M, Karakashev D, Angelidaki I. Integrated production of cellulosic bioethanol and succinic acid from industrial hemp in a biorefinery concept. Bioresour Technol 2016;200:639–47.
[297] Dürre P. Biobutanol: an attractive biofuel. Biotechnol J: Healthcare Nutr Technol 2007;2:1525–34.
[298] Zhang C, Li T, Su G, He J. Enhanced direct fermentation from food waste to butanol and hydrogen by an amylolytic *Clostridium*. Renew Energy 2020;153:522–9.
[299] Grana R, Frassoldati A, Faravelli T, Niemann U, Ranzi E, Seiser R, et al. An experimental and kinetic modeling study of combustion of isomers of butanol. Combust Flame 2010;157:2137–54.
[300] Ndaba B, Chiyanzu I, Marx S. n-Butanol derived from biochemical and chemical routes: a review. Biotechnol Rep 2015;8:1–9.
[301] Trindade WRdS, dos Santos RG. Review on the characteristics of butanol, its production and use as fuel in internal combustion engines. Renew Sustain Energy Rev 2017;69:642–51.
[302] Sukumaran RK, Gottumukkala LD, Rajasree K, Alex D, Pandey A. Butanol fuel from biomass: revisiting ABE fermentation. In: Pandey A, Larroche C, Ricke SC, Dussap C-G, Gnansounou E, editors. Biofuels: Elsevier; 2011. p. 571–86.
[303] Fernbach A, Strange EH. Fermentation process for the production of acetone and higher alcohols from starch, sugars, and other carbohydrate material. Google Patents; 1912. https://patents.google.com/patent/US1044368A/en.
[304] Nanda S, Dalai A, Kozinski J. Butanol and ethanol production from lignocellulosic feedstock: biomass pretreatment and bioconversion. Energy Sci Eng 2014;2:138–48.
[305] Jiang Y, Liu J, Jiang W, Yang Y, Yang S. Current status and prospects of industrial bio-production of n-butanol in China. Biotechnol Adv 2015;33:1493–501.
[306] Wang Z, Cao X, Li N, Yang Z, Lei M, Zhao Y, et al. Production of butanol directly from hemicellulose through secretory expression of a xylanase in *Clostridium acetobutylicum*. Energy Fuels 2020;34:3376–82.
[307] Reddy LV, Veda AS, Wee YJ. Utilization of banana crop residue as an agricultural bioresource for the production of acetone-butanol-ethanol by *Clostridium beijerinckii* YVU1. Lett Appl Microbiol 2020;70:36–41.
[308] Seifollahi M, Amiri H. Enhanced production of cellulosic butanol by simultaneous co-saccharification and fermentation of water-soluble cellulose oligomers obtained by chemical hydrolysis. Fuel 2020;263:116759.
[309] Tucki K, Orynycz O, Wasiak A, Świć A, Mruk R, Botwińska K. Estimation of carbon dioxide emissions from a diesel engine powered by lignocellulose derived fuel for better management of fuel production. Energies 2020;13:561.
[310] Dharmaraja J, Shobana S, Arvindnarayan S, Vadivel M, Atabani A, Pugazhendhi A, et al. Biobutanol from lignocellulosic biomass: bioprocess strategies. In: Yousuf A, Pirozzi D, Sannino F, editors. Lignocellulosic biomass to liquid biofuels. Elsevier; 2020. p. 169–93.
[311] Cao X, Chen Z, Liang L, Guo L, Jiang Z, Tang F, et al. Co-valorization of paper mill sludge and corn steep liquor for enhanced n-butanol production with *Clostridium tyrobutyricum* Δcat1:: adhE2. Bioresour Technol 2020;296:122347.
[312] Itelima J, Bang W, Onyimba I, Oj E. A review: biofertilizer; a key player in enhancing soil fertility and crop productivity. J Microbiol Biotechnol Rep 2018;2:22–8.
[313] Bhardwaj D, Ansari MW, Sahoo RK, Tuteja N. Biofertilizers function as key player in sustainable agriculture by improving soil fertility, plant tolerance and crop productivity. Microb Cell Factories 2014;13:66.
[314] Khayum N, Anbarasu S, Murugan S. Biogas potential from spent tea waste: a laboratory scale investigation of co-digestion with cow manure. Energy 2018;165:760–8.
[315] Kuan KB, Othman R, Rahim KA, Shamsuddin ZH. Plant growth-promoting rhizobacteria inoculation to enhance vegetative growth, nitrogen fixation and nitrogen remobilisation of maize under greenhouse conditions. PloS One 2016;11:e0152478.
[316] Ahemad M, Kibret M. Mechanisms and applications of plant growth promoting rhizobacteria: current perspective. J King Saud Univ Sci 2014;26:1–20.
[317] Owamah H, Dahunsi S, Oranusi U, Alfa M. Fertilizer and sanitary quality of digestate biofertilizer from the co-digestion of food waste and human excreta. Waste Manag 2014;34:747–52.
[318] Barzee TJ, Edalati A, El-Mashad H, Wang D, Scow K, Zhang R. Digestate biofertilizers support similar or higher tomato yields and quality than mineral fertilizer in a subsurface drip fertigation system. Front Sustain Food Syst 2019;3:58.
[319] Motte J-C, Sambusiti C, Dumas C, Barakat A. Combination of dry dark fermentation and mechanical pretreatment for lignocellulosic deconstruction: an innovative strategy for biofuels and volatile fatty acids recovery. Appl Energy 2015;147:67–73.
[320] Castilla-Archilla J, O'Flaherty V, Lens PNL. Biorefineries: industrial innovation and tendencies. In: Bastidas-Oyanedel J-R, Schmidt JE, editors. Biorefinery. Switzerland: Springer Nature; 2019. p. 3–35.
[321] Slezak R, Grzelak J, Krzystek L, Ledakowicz S. Production of volatile fatty acids and H_2 for different ratio of inoculum to kitchen waste. Environ Technol 2019:1–11. https://doi.org/10.1080/09593330.2019.1619847.
[322] Chalima A, Oliver L, Fernández de Castro L, Karnaouri A, Dietrich T, Topakas E. Utilization of volatile fatty acids from microalgae for the production of high added value compounds. Fermentatio 2017;3:54.
[323] Da Ros C, Conca V, Eusebi AL, Frison N, Fatone F. Sieving of municipal wastewater and recovery of bio-based volatile fatty acids at pilot scale. Water Res 2020;174:115633.
[324] Tamis J, Mulders M, Dijkman H, Rozendal R, van Loosdrecht MC, Kleerebezem R. Pilot-Scale Polyhydroxyalkanoate production from paper mill wastewater: process characteristics and identification of bottlenecks for full-scale implementation. J Environ Eng 2018;144:04018107.
[325] Chalima A, Hatzidaki A, Karnaouri A, Topakas E. Integration of a dark fermentation effluent in a microalgal-based biorefinery for the production of high-added value omega-3 fatty acids. Appl Energy 2019;241:130–8.
[326] IEA Bioenergy. IEA Bioenergy Task 42 Biorefinery. *Sustainable and synergetic processing of biomass into marketable food & feed ingredients, products (chemicals, materials) and energy (fuels, power, heat)*. IEA Bioenergy; 2014. https://www.ieabioenergy.com/wp-content/uploads/2014/09/IEA-Bioenergy-Task42-Biorefining-Brochure-SEP2014_LR.pdf. [Accessed 23 March 2020].
[327] IEA Bioenergy. Bio-based chemicals A 2020 update. IEA Bioenergy; 2020. March 25 2020, https://www.ieabioenergy.com/wp-content/uploads/2020/02/Bio-based-chemicals-a-2020-update-final-200213.pdf.
[328] Lackner M. Bioplastics - biobased plastics as renewable and/or biodegradable alternatives to petroplastics. In: Othmer K, editor. Kirk-othmer encyclopedia of chemical technology. sixth ed. Hoboken, New Jersey: Wiley; 2015. p. 896.
[329] Vogt W. Digging into the science of cellulosic ethanol. Farm Progress; 2015. https://www.farmprogress.com/biofuel/digging-science-cellulosic-ethanol. [Accessed 23 March 2020].
[330] Vetere M. NatureWorks opens lab to turn methane into PLA. European Bioplastics; 2016. https://www.european-bioplastics.org/natureworks-opens-lab-to-turn-methane-into-pla/. [Accessed 23 March 2020].
[331] Höltinger S, Schmidt J, Schmid E. The green biorefinery concept: optimal plant locations and sizes for Austria. Jahrbuch der ÖGA (Österreichische Gesellschaft für Agrarökonomie) 2012;21:147–56.
[332] Group L. Annual report 2017. https://www.lenzing.com/index.php?type=88245&tx_filedownloads_file%5bfileName%5d=fileadmin/content/PDF/07_Finanzen/Geschaeftsberichte/EN/GB_2017_EN.pdf. [Accessed 23 March 2020].
[333] Lignol innovations ltd. March 23 2020, https://www.offsetters.ca/t/lib/pdf/projects/lignol-innovations-ltd.pdf.
[334] Biobased Economy. Survey of the biorefinery programmes in The Netherlands. Biobased Economy. March 23 2020, https://www.biobasedeconomy.nl/wp-content/uploads/2014/09/Survey-Biorefineries-programmes-in-The-Netherlands-270814.pdf.
[335] Blog B. The pilot-scale integrated biorefinery of algenol. Biorrefineria; 2016. March 23 2020, https://biorrefineria.blogspot.com/2016/05/the-pilot-scale-algae-integrated-biorefinery-algenol.html.
[336] Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R, et al. Toward a common classification approach for biorefinery systems. Biofuel Bioprod Biorefin 2009;3:534–46.
[337] Scopus. www.scopus.com. [Accessed 1 April 2020].