Chapter 20

Volatile Fatty Acid Production from Anaerobic Digestion of Organic Residues

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Abstract

Short chain volatile fatty acids (VFAs) from acetic acid (C2) to valeric acid (C5) are important starting chemicals for chemical industry. The production of VFAs from rejected resources (organic residues) using self-sustaining technologies has an exciting potential in supporting the US chemical industry to achieve the goal that 20% of chemicals produced in the USA will be bio-based. Acidogenic anaerobic digestion as a robust, well-established, and versatile biological technology can be applied as an alternative approach for the valorization of organic residues (municipal, agricultural, and industrial wastes) by the production of VFAs. In a typical acidogenic anaerobic digestion operation, residue type, pretreatment, reactor operation, and VFA recovery are the key factors that influence VFA production. This chapter discusses these factors and provides an experimental approach of VFA production from organic residues.

Key words Acidogenic anaerobic digestion, Organic residue, Volatile fatty acids, Liquid–liquid extraction

1 Introduction

Anaerobic digestion is an established technology for the treatment of domestic, industrial and agricultural residues, which also generates value added products such as methane, hydrogen, and organic acids [1]. Many classes of bacteria play important role in this complex biological process, which is composed of sequential steps, namely; hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These steps can be engineeringly separated into two phases to enhance digestion efficiencies and produce different chemical products. In the first phase, anaerobic bacteria generate VFA metabolites as value-added chemicals via steps of hydrolysis, acidogenesis, and acetogenesis. The VFA intermediates are further converted to methane and carbon dioxide by archaea in the second phase (methanogenesis, or "methane fermentation") to achieve waste stabilization.

Venkatesh Balan (ed.), *Microbial Lipid Production: Methods and Protocols*, Methods in Molecular Biology, vol. 1995, https://doi.org/10.1007/978-1-4939-9484-7_20,

It is apparent that acidification phase of the anaerobic digestion is the target stage for VFA production [2]. During the acidification phase, the hydrolysis first takes place to convert various carbon substrates to energy (ATP), reducing agents, and monomers. It has been widely reported that *Bacteroidetes* are a key microbial group that plays a substantial role in the hydrolysis stage to degrade primary carbon polymers [3, 4]. The intermediate compounds from the hydrolysis step are then fermented by acidogens and acetogens through the glycolytic pathway to produce short chain VFAs (acetic, propionic, and butyric acids). *Synergistetes* and *Clostridium* are the representative bacteria in anaerobic digestion process that carry out such transformations [3, 5, 6]. However, during conventional anaerobic digestion process, VFAs as the substrates for archaeal metabolism are used for methane production. In order to accumulate them, digestion conditions need to be adjusted to inhibit or eliminate methanogens during the digestion.

1.1 Effects of Organic Wastes and Their Pretreatment in VFA Production

A large variety of organic residues has been investigated for VFA production. They include both solid and liquid streams, particularly the organic fraction of municipal solid waste, municipal sludge (both primary and waste activated sludge), food and food processing wastes, crop residues, and livestock wastes. For instance, organic wastes from the sugar industry (beet pulp) and wastewater mixture was processed in a continuously mixed anaerobic acidification process, which resulted in 43.8–52.9% acidification of initial chemical oxygen demand (COD) [2]. The sulfite spent liquor from the pulp and paper industry was used by a completely mixed stirred tank reactor (CSTR) to produce VFAs [7]. The maximum VFA concentration reached 7.0 g COD equivalent/L with the degree of acidification of 36%. Various mixtures of different organic wastes had been studied aiming to promote a higher production of VFA. Dogan et al. [8] and Erguder and Demirer [9] evaluated the potential of high-rate anaerobic acidification of high solids containing substrates (organic fraction of municipal solid waste and cow manure) for the VFA production in leaching bed reactors (LBRs). The maximum VFA concentration (mainly acetic and butyric acids) was around 6 g/L (acetic acid equivalent). Ma et al. [10] mixed potato peel waste, food waste, and waste activated sludge to run a cofermentation to improve anaerobic acidification of VFA production. The results revealed that acetate was the most dominant VFA, making up 41.3–57.6% of the total VFAs produced during acidification under alkaline condition. The concentrations of propionate and valerate decreased dramatically once more potato peel waste was added. It was also observed that starch in the food wastes favored butyric acid accumulation, while increase of lipids and protein in the feed enhanced the synthesis of valerate and propionate.

Due to the complex composition of organic residues and wastes such as sludge, food waste, and organic fraction of municipal solid

waste, hydrolysis is the rate-limiting step for the anaerobic digestion. Various pretreatment methods have been explored to enhance the solubilization of these wastes, which include chemical, biological, thermal, physical, and combined approaches [11]. Chemical methods use acid and alkali, or strong oxidizing agent (i.e., ozone and hydrogen peroxide) to achieve the solubilization of polymeric substances in organic residues and wastes. Biological pretreatment applies enzymes and microbes that degrade cell walls and large polymer and consequently realize the solubilization of the residues and wastes. Compared to chemical and biological pretreatment, thermal treatment is a simple and economical method to achieve the solubilization by breaking hydrogen and other chemical bonds of the substances in the residues and wastes. Ultrasonic treatment as a physical process has also been intensively studied to break down polymeric structure of substances. In addition, the pretreatment efficiency of the organic wastes was improved using the combination of different pretreatment methods. For example, alkali and ultrasonics were integrated to treat food wastes; hydrogen peroxide and microwave were combined to treat municipal solid wastes.

1.2 VFA Accumulation by Acidogenic Anaerobic Digestion

Anaerobic acidification relies on the establishment of environmental and operational conditions that favor growth of acidogenic microbes, while preventing methanogenic activity. There are many methods to achieve anaerobic acidification, such as chemical inhibition of methanogens, heat treatment of sludge, inoculation of bacteria, and adjustment of digestion parameters [11]. Considering both technical soundness and economical feasibility, the adjustment of digestion parameters is a practical approach to realize anaerobic acidification. It has been reported that pH, solids retention time (SRT), temperature, and organic loading rate (OLR) are the key operational parameters that influence anaerobic VFA production (Table 1) [11, 12].

Preferred pH values for the VFA production vary with the type of wastes and are in the range of 5.25–11.0 [13]. Alkaline pH (from 8 to 11) is preferred once municipal sludge is used as the feed [14]. The alkaline condition enhances hydrolysis of the sludge through ionization of the charged groups (e.g., carboxylic groups) of the extracellular polymeric substances in the sludge. Neutral pH values (around 7) lead to high solubilization of carbohydrates, proteins, and lipids, and consequently good VFA production from kitchen wastes [15]. pH control influences the composition of VFA mixtures produced in anaerobic acidification [16]. pH 6–6.5 favored accumulation of acetic and butyric acids from dairy wastewater, while propionic acid production was observed in the pH range of 4–4.5 [17, 18]. As for glucose-rich medium, acidic and alkaline conditions were favorable for accumulation of acetic and butyric acids, respectively [19].

Table 1
VFA concentrations and production yields (modified from Lee et al. [11] and Cavinato et al. [12])

Feedstock	HRT (d)	OLR (kg VS/m^3·d)	Temperature (°C)	VFA Conc. (g VFA/L)	VFA yield (g VFA/kg COD)	Reference
Cheese whey	2.1	–	37	0.84	–	[54]
OFMSW	3.5	16	55	13.8	263	[36]
Food waste	3.0	16.8	55	12.3	221	[34]
Fruit/vegetable waste	1–11	11–102	37	7.6–28.5	33–279	[30]
Food waste + sludge	8.92	8.31	35	24.1	–	[55]
OFMSW+WAS	3.3	18	55	8.1	137	[56]
Palm oil mill effluent	4.0	–	30	15.3	–	[57]
OFMSW	6	4.1	23	9.5	127	[26]
Gelatin-rich proteinaceous Wastewater	0.5	–	37	1.57	–	[31]
WAS	4.6–5.9	1.2–1.9	35	3.2–7.5	207–325	[29]
Sugar industry wastewater + pressed beet pulp	2	–	35	3.64	–	[2]
Olive oil mill effluent	1.4	–	25	10.7	–	[58]

It has been reported that reducing solids retention time (SRT) can actively promote the production of VFA [20, 21]. Shorter SRTs limit the growth of methanogens in anaerobic digestion, so that acidogenic bacteria dominate the culture resulting in accumulation of VFAs [22, 23]. Numerous studies demonstrated that 2–15 days are the preferred SRTs on a variety of feedstocks to increase VFA production [2, 16, 18, 24, 25].

Temperature has a significant impact on anaerobic acidification. It has been reported that VFA production from waste occurred at a wide temperature range from psychrophilic (4–20 °C) [26–28] to mesophilic (20–50 °C) [7, 9, 17, 28–31] to thermophilic (50–60 °C) [32–34] and extreme/hyperthermophilic (60–80 °C) [24, 35] conditions. It has been demonstrated that increasing the temperature within the psychrophilic and mesophilic conditions is generally beneficial for the accumulation of VFAs.

Organic loading rate (OLR) is another important operational parameter for anaerobic VFA production [17, 22, 36] and it is linked with type of organic residues [11]. The VFA production from starch-based wastewater was increased proportionally with the increase of OLR from 1 g COD/L/d to 32 g COD/L/d

[37]. While, the VFA production from olive oil mill residue in the OLR range of 3.2–15.1 g COD/L/d demonstrated that the highest VFA concentration was obtained at the OLR of 12.9 g COD/L/d [38]. It has also been reported that feeding frequency influences the VFA production [11].

The aforementioned operational parameters have been combined to synergistically enhance VFA accumulation. Sans et al. [39] studied the effects of different OLRs (22.4–85.2 kg VS/m^3/d), retention times (8 h to 8 days), and sludge recirculation (related with SRT) on mesophilic (37 °C) anaerobic acidification of solid food wastes. The results showed that the highest VFA concentration of 23.1 g/L was reached with retention time of 6 days and high OLRs without sludge recirculation. Acetic and butyric acids are the major VFAs in this study. Dogan and Demirer [25] investigated the combined effects of OLR and pH on VFA production from organic fraction of municipal solid waste using completely stirred tank reactors (CSTRs). The study concluded that the maximum VFA production was observed at OLR of 20 g VS/L/d and HRT of 2 days with a pH value of 5.5. Meanwhile, they also demonstrated that selective production of organic acids was possible during the digestion by controlling the OLR and pH. Higher OLRs and lower pH enhanced the acetic acid production and reduced butyric acid production. Jankowska et al. [16] investigated the impact of pH (4–12) and retention times (5–15 days) on anaerobic acidification of primary sludge and waste activated sludge from a municipal wastewater treatment plant. The conditions of the short retention time (5 days) with low pH (4) and the long retention time (15 days) with high pH (10) were in favor of VFA accumulation. The highest VFA concentration was achieved from the condition of 15 days retention time at pH 10 (0.62 g/g VS). Jiang et al. [17] studied the effects of pH, temperature, and organic loading rate (OLR) on anaerobic acidification of food waste. The results indicated that under the culture conditions of low OLR (5 g TS/L/d), slightly acidic pH (6), and mesophilic temperature (35–45 °C), the acidification of food waste produced 39.5 g/L of VFAs with a yield of 0.504 g VFAs/g VS fed. Acetic and butyric acids were the predominant acids accounting for 77% of total VFAs.

1.3 Recovery of VFA from the Anaerobic Digestion Broth

Due to the complicated composition of the broth of anaerobic acidification, the major technical and economic barrier of using VFAs is their recovery, separation, and purification [40–43]. Numerous studies have been conducted to address this challenge [41, 44]. Techniques such as electrodialysis [45], ion exchange [42], adsorption [46], and liquid–liquid extraction [47] have been intensively investigated to recover VFAs from the broth. Liquid–liquid extraction among these methods is widely considered an efficient, economical, and environmentally sound method for the recovery of carboxylic acids [48]. The efficiency of VFA

recovery during the liquid–liquid extraction highly depends on the nature of the VFAs, the concentration of the solvent (extractant), the type of diluent [49], and pH [50]. Alcohols, ketones, ethers, aliphatic hydrocarbons, and organophosphates are the solvents widely used for the extraction. Compared to the other solvents, organophosphates such as trioctylphosphine oxide (TOPO) and tri-n-butyl phosphate (TBP) have much larger distribution coefficient for carboxylic acids [51], so they are the better solvents for VFA extraction and recovery. Alkaya et al. [52] investigated the anaerobic acidification of sugar beet processing wastes and subsequent liquid–liquid extraction of the resulted VFAs. The influence of pH and the extractant (TOPO in kerosene) concentrations on the recovery of VFAs from fermentation broth were evaluated. The results indicated that TOPO concentration and pH were the crucial factors that influence VFA extraction efficiency. pH 2.5 was determined as the optimal pH for the extraction. Increase of TOPO concentration in kerosene significantly improved the extraction efficiency. Higher VFA recoveries (60.7–97.6%) were achieved at 20% TOPO in kerosene at pH 2.5.

2 Materials

2.1 Feedstock

The wastes and wastewater could be animal manure/wastewater, food wastes, municipal sewage sludge, and industrial organic wastes/wastewater. The feedstocks need to have a moisture content 85% or more.

2.2 Basal Medium (BM)

The BM contained the following chemicals to supply the necessary nutrients for optimum anaerobic microbial growth (concentrations are given in parentheses):NH_4Cl (1200 mg/L), $MgSO_4{\cdot}7H_2O$ (400 mg/L), KCl (400 mg/L), $Na_2S{\cdot}9H_2O$ (300 mg/L), $CaCl_2{\cdot}2H_2O$ (50 mg/L), $(NH_4)_2{\cdot}HPO_4$ (80 mg/L), $FeCl_2{\cdot}4H_2O$ (40 mg/L), $CoCl_2{\cdot}6H_2O$ (10 mg/L), KI (10 mg/L), $MnCl_2{\cdot}4H_2O$ (0.5 mg/L), $CuCl_2{\cdot}2H_2O$ (0.5 mg/L), $ZnCl_2$ (0.5 mg/L), $AlCl_3{\cdot}6H_2O$ (0.5 mg/L), $NaMoO_4{\cdot}2H_2O$ (0.5 mg/L), H_3BO_3 (0.5 mg/L), $NiCl_2{\cdot}6H_2O$ (0.5 mg/L), $NaWO_4{\cdot}2H_2O$ (0.5 mg/L), and cysteine (10 mg/L) [53].

3 Methods

VFA production from organic residues requires bench or pilot scale tests to evaluate the acidification performance under different digestion conditions (pH, temperature, organic loading rate, and hydraulic and solids retention time). Typical steps for such a feasibility and performance study are described as follows:

3.1 Characterization of Feedstock

1. Homogenize the feedstock (liquid) using a commercial blender to vigorously mix prior to its compositional analyses (*see* **Note 1**).
2. Analyze the feedstock to determine the total and soluble COD, total and total volatile solids (TS and TVS), total Kjeldahl nitrogen (TKN), total phosphorus (TP), total ammonium nitrogen (TAN), pH, and alkalinity using the standard methods [24] (*see* **Note 2**).
3. Store the feedstock at −20 °C until it is used.

3.2 Inoculation

1. Obtain a mixed anaerobic culture from an anaerobic digester operating in full scale (*see* **Note 3**).
2. Allow the culture to settle down for 24 h to increase the number of microorganisms.
3. Discard the supernatant and use the settlings to inoculate the digester.
4. Use the basal medium as a part of daily feeding in addition to the feedstock (substrate) to provide micronutrients and macronutrients, minerals, and vitamins for microorganism activities.
5. Make the total solids content of the solution in the digester and the feed at 5% (w/w).

3.3 Operation of Anaerobic Reactors and Monitoring

1. Decide the operational mode (batch, semicontinuous, or continuous) of the digester and decide a feeding schedule based on the operational mode.
2. Specify the reactor operation such as, hydraulic retention time, pH, organic loading rate, temperature, mixing rate (*see* **Note 4**).
3. Monitor biogas production, pH, VFA concentration, soluble COD, TS, and TVS during the test (*see* **Note 5**).
4. Establish a steady-state condition of the digestion following the start-up period regarding stabilization of biogas production and sCOD reduction.
5. Monitor sCOD reduction to VFAs (degree of acidification) in the steady-state digestion to evaluate performance of the acidification (*see* **Note 6**).

3.4 Liquid–Liquid Extraction of VFA from Anaerobic Broth

1. Prepare 20% by weight trioctylphosphine oxide (TOPO) solution in kerosene at 30 °C.
2. Collect the supernatant from the anaerobic digester and adjust pH to 2.5.
3. Mix the collected supernatant from the anaerobic digester with TOPO in kerosene with a volumetric ratio of 1:3.
4. Mixed vigorously the supernatant and solvent for 5 min and then allowed to separate by gravity for 3 min (This cycle needs to repeat three times to improve the extraction efficiency).

5. Analyze VFAs left in the aqueous phase after the extraction using gas chromatography (GC) (*see* the **Note 5**).
6. Calculate the partition of VFAs in aqueous and organic solvent and report the extraction efficiency (*see* **Note 7**).

4 Notes

1. The blended waste and wastewater will be resuspended to pass a screen (1–2 mm opening). The solution collected after the screening is used as the substrate to carry out the culture.
2. Standard methods for wastewater analyses are adopted in this part. The total and soluble CODs are measured by a closed reflux colorimetric method (Method no 5220-D). TS and TVS concentrations are measured gravimetrically following Methods 2540B and 2540E, respectively. Total Kjeldahl nitrogen (TKN) is measured using Method 4500-N_{org}-B, total phosphorus (TP) is measured by Method 4500-P, and total ammonium nitrogen (TAN) concentration is measured by Method 4500-NH_3. pH is measured by electrochemical method (Method 4500-H+), and alkalinity is measured by titration method (Method 2320).
3. Anaerobic digestate from municipal/industrial wastewater treatment plants can be used as the seed.
4. All reactors should be operated in triplicates for statistical interpretations of the results.
5. The gas production in the digesters is measured by water displacement setup. The biogas compositions are measured via GC equipped with Thermal Conductivity Detector (TCD). Methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), oxygen (O_2), and hydrogen (H_2) are separated with two series of columns with injector and detector temperature of 50 °C and 80 °C, respectively. Helium gas is used as the carrier at 100 kPa constant pressure 45 °C of oven temperature. VFA measurements are carried out using GC with flame ionization detector (FID). The samples are filtered through 0.45 μm online filters, and their pH are lowered to 2.5 by formic acid prior to their injection to GC column. The GC oven temperature is increased from 100 °C to 200 °C by 8 °C/min ramping. Inlet and detector temperatures are 250 and 280 °C respectively. Helium is again used as a carrier gas with a flow rate of 6 mL/min.
6. Degree of acidification = $(S_f/S_i)\times 100$, where S_i is the initial concentration of sCOD (mg/L), S_f is the produced VFAs expressed as theoretical equivalents of sCOD (mg/L) concentrations.

7. Partition of VFAs in organic solvent and aqueous phases at equilibrium can be calculated using the equation of $K_d = ([VFA]_{org})/([VFA]_{aq})_{eq}$, where $[VFA]_{org}$ and $[VFA]_{aq}$ are the concentrations of VFA in organic solvent and water, respectively. K_d is the partition coefficient without a unit.

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