Kinetics of volatile fatty acids and hydrogen production during anaerobic digestion of organic waste material

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This paper describes the changes in volatile fatty acids and hydrogen production in time, during an anaerobic digestion process of organic waste material. The experiment showed that the reaction run most efficiently between 6 and 12th hour of the reaction time. This can be an indicator for future experiments on volatile fatty acids and hydrogen production optimisation.
Key words: biopolymers, anaerobic digestion, VFA, hydrogen.

Introduction

Every year the disposal of municipal solid wastes (MSW) poses serious environmental and economic problems, especially in fast developing countries. Nearly 1600 million tons of MSW per year is generated worldwide with up to 43% contributed by Asia and Oceania and 28% contributed by North America and the European Union [1]. In developing countries approximately 50% of MSW is biodegradable [2]. These issues, together with price increases and supply disturbances affecting petroleum products and natural gas, have led to research into alternative fuel sources. One of the biotechnologies developed to utilize the organic fraction of MSW for useful energy and materials recovery is a two-phase anaerobic digestion [3]. The organic compounds are decomposed into a microbial chain to volatile fatty acids (VFA) during the first stage and then, in the second stage, the acids are decomposed into methane and carbon dioxide [4]. Acidogenic bacteria of the first phase convert carbohydrates mainly into acetic, propionic and butyric acids [5, 6]. These acids are then used to produce biogas in the second stage of anaerobic digestion.

In addition, under anaerobic conditions hydrogen can be produced as a by-product during the conversion of organic wastes into organic acids (the first phase of anaerobic digestion). This valuable fuel can be produced either from the organic fraction of municipal solid wastes (OFMSW) or from industrial wastes [7]. The process is carried out by fermentative H_2-producing microorganisms, such as facultative and obligate anaerobes [8,9]. Microorganisms use the VFA gained over the first phase, which are mainly acetic, lactic and butyric acids [10]. Microbial consortia present in waste activated sludge become a valuable inoculum for such processes [11]. Principally, because it is a cheap source of fermenting bacteria, including not only acidogens, which are crucial in terms of VFA or hydrogen generation, but also methanogens. To eliminate the latter from the reaction mixture and direct the process to VFA or H_2 production, a heat shock pretreatment of inocula in boiling water is used [11]. Moreover, keeping the pH of the cultures in the acidogenic range (5.8–6.5) or monitoring the chemical oxygen demand (COD) are the most common methods to gain the highest products concentration [4,12,13]. According to scientific reports, hydrogen is safe, versatile, has a high energy content and high utilization efficiency [14]. Hydrogen is a more desired energy source than methane, due to the production of CO_2 which is known to contribute to the greenhouse effect [15]. Although the rate of H_2 production is low and the technology for this process needs further development, this is a future "green energy" source [16].

The aforementioned useful applications of volatile fatty acids are only a part of much broader spectrum. Apart from being a substrate for biogas or hydrogen production, VFA found applications in electricity, biological nutrient removal or formation of lipids for biodiesel [17]. Volatile fatty acids can also be utilized and polymerized into polyhydroxyalkanoate (PHA) by bacteria under unbalanced growth conditions such as nitrogen limitation [18]. The main obstacle to a PHA application is its high production cost. The production of PHA from organic wastes may significantly reduce the production cost because of the negative raw material cost and less sludge produced when it is integrated into a biological waste treatment system [19,20].

The aim of this work was to examine the kinetics of VFA and hydrogen production in time, during anaerobic degradation of the organic waste material.

Materials and Methods

The substrate used in this experiment was expired food taken from the local market. Digested sludge from the Municipal Wastewater Treatment Plant in Łódź served as inoculum. The inoculum was characterised by 2 parameters: total solids and volatile solids, which was 30.3 g/L and 19.43 g/L, respectively. The experiment was performed in 500-ml bottles. Before the experiment started, the sludge was being heated in 70°C for 30 minutes [21].

The experiment was conducted in an anaerobic environment in a temperature of 37°C for 24 hours. Before the start of the reaction, the bottles were flushed with nitrogen to guarantee the anaerobic conditions. In the course of the experiment, samples were taken, using a syringe, to measure the gas composition (CH_4, CO_2, H_2), pH and VFA composition. The scheme of the experimental set up is shown in Figure 1.

Volatile fatty acids were measured through steam distillation with the BÜCHI B-324 Instrument. The concentration of gases was measured with a gas chromatograph (GC-8610C, SRI Instruments, USA) equipped with a thermal conductivity detector (TCD). The temperatures of the column and detector were set at 60°C and 150°C, respectively. Helium was used as the carrier gas at a flow rate of 10 mL/min. A silica gel column (1 m) with a molecular sieve 80/100 was applied in this approach. pH analyses were conducted using a pH-meter electrode WTW pH 540 GLP. All analytical procedures were performed in accordance with the Standard Methods (APHA–AWWA, 1992).

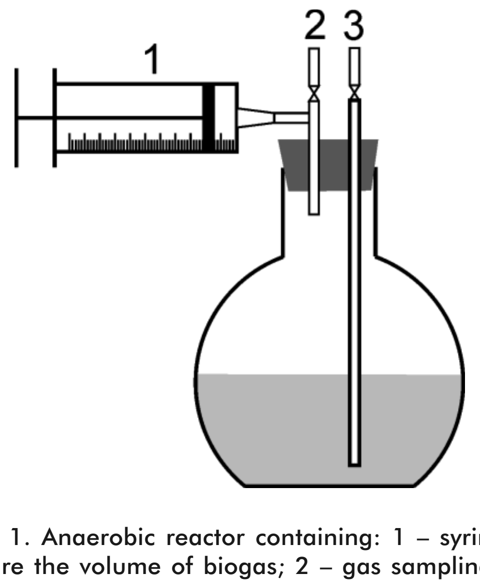

Figure 1. Anaerobic reactor containing: 1 – syringe to measure the volume of biogas; 2 – gas sampling line; 3 – sludge sampling

Two sets of the experiment were done. The first one containing only the sludge (Set 1), and the second one with a mixture of sludge and 8.8 g dry weight/L of a substrate (Set 2). Each was performed in duplicate and the average data were then discussed. To measure the fluctuation of VFA, pH and H_2 in time, samples were taken every 3 hours, e.g.: at 0h, 3h, 6h, 9h, 12h and after 24 hours. The data collected are shown in Figure 2.

Results and Discussion

In this paper, the time-dependent fatty acid concentration, VFA production rate, substrate pH, and product gas composition will be presented and discussed.

The data collected from the pH measurements are shown in Figure 3.

The figures presented in Figure 2 clearly show that in the reaction performed with OFMSW, the amount of VFA is increasing along with time. In contrast, in Set 1 the concentration of fatty acids stays on a relatively constant level and the values range between 1020 and 1548 $mgCH_3$

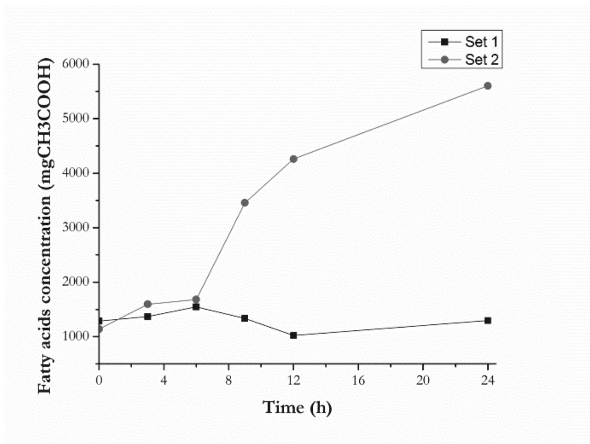

Figure 2. Comparison of volatile fatty acids production in two different experimental sets, measured at selected time instants

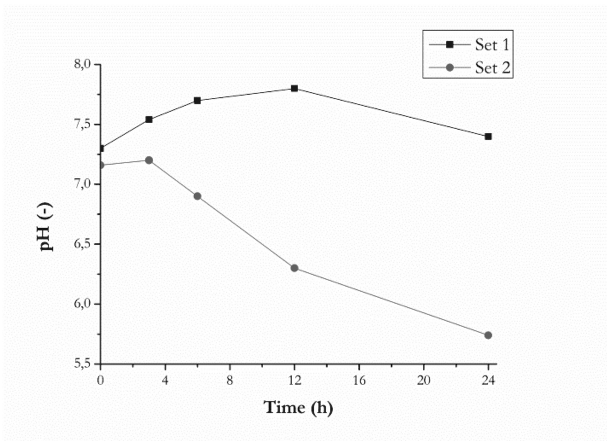

Figure 3. PH of the reacting mixture at selected time instants

COOH/dm^3. After the 24h of the reaction, the concentration of VFA in Set 2 reaches 5600 mgCH_3COOH/dm^3, which is almost six times more than the maximal amount of the volatile fatty acids gained in total in Set 1. During the first 6 hours of dark fermentation the production rate of volatile fatty acids was very low. This is caused by the phase of adaptation of microbes to the new substrate. The highest production rate of VFA was detected between the 6th and the 12th hour of the process. The data obtained allow the evaluation of the actual VFA production reached after the microbial digestion of organic wastes.

Simultaneously with VFA, the pH values were measured. The data are shown in Figure 3. A falling trend can be clearly seen in the pH of both sets of the experiment. However, in the samples with the initially added organic matter (set 2), the pH dropped more drastically, reaching 5.74 after 24 hours of the experiment. This observation can be an additional confirmation of the faster fermentation processes in the second set. This is due to the higher amount of VFA produced also in set 2. It is known that intensive VFA production reflects in fast pH drops in a sample. Numerous authors have proven that the best pH range for the production of acetic, propionic or butyric acids is between 5 and 7. [22,23,24] Elefsiniotis et al. [25] generated VFA from an anaerobic digester treated with a mix of starch-rich industrial and municipal wastewater. He evidenced that naturally-produced VFA are generated in the highest concentrations at a pH from 5.45 to 6.68. Lee et al. [17] described in his review an interesting observation: the optimal pH values for the production of VFA are mainly in the range of 5.25–11, but specific ranges are dependent on the type of waste used. Switching the substrate from organic wastes into the sludge reflects also in the optimal pH switch from acetic to alkaline (pH 8-11). A similar situation is confirmed in the aforementioned data, where the pH of Set 1 was recognized to be 7-8.

The second parameter measured in the present experiment was the production efficiency of gases: CH_4, CO_2, H_2 during the reaction time. Figure 4 shows only the data of Set 2. It is because the volume of the produced gases in Set 1 was below the detection limit. In the second set of the experiment hydrogen and carbon dioxide were detected. After the 6th hour of the process, low amounts of CO_2 and H_2 were measured: 30.6 mL and 16 mL, respectively. The highest gases production was described between the 6th and the 9th hour of the reaction time and it reached 242 mL for CO_2 and 115.2 mL for H_2. For the rest of the time, the volume of the mentioned gases remained on a stable, similar level, reaching 255 mL for CO_2 and 120 mL for H_2 at the 24th hour of the experiment. CH_4 was not produced. This observation confirms that acidogenic bacteria are the most active in the first hours of the fermentation. The methanogens activity is confirmed to be stopped due to the boiling of the samples in hot water.

To visualize the kinetics of hydrogen production during the dark fermentation processes, the most common is to apply the Gompertz equation [29,30]. The Gompertz formula is as follows:

$$H = P \cdot \exp\left\{-\exp\left[\frac{R_M \cdot e}{P}(\lambda - t)+1\right]\right\}$$

where:
H – summarized production of H_2 (mL),
P – production potential of H_2 (ml),
R_M – maximal production rate H_2 (ml·h^{-1}),
– lag-phase duration (h),
t – time (h),
e – e number (2.7182)

Figure 4 presents the result of fitting the experimental data into the equation. The proposed equation describes the experimental data (R^2=1) very well.

In the scope of volatile fatty acids production, the presented analyses show that the whole 24-hour period of the experiment is crucial , whereas hydrogen is most dynamically produced up to the 9th hour of the anaerobic reaction. Comparing, however, the process of VFA production from OFMSW and from the sludge, we can see that there is a visible difference in the dynamics of the reaction. While in Set 1 the VFA amount is on a similar detection level throughout the whole 24-hour experiment, however, it reaches the maximum in the 6th hour of the reaction. At the same time, in Set 2 the amount of fatty acids visibly jumped up after the 6th hour and was growing up to the 24th hour of the process. The results presented above correspond with the conclusions of other research groups. According to Bengtsson et al. [26] the application of a higher hydraulic retention time (HRT) could be advantageous to the production of VFA from OFMSW as the microorganisms have more time to react with waste. A prolonged HRT, however, could also lead to stagnant VFA production. For instance, the production of VFA from dairy

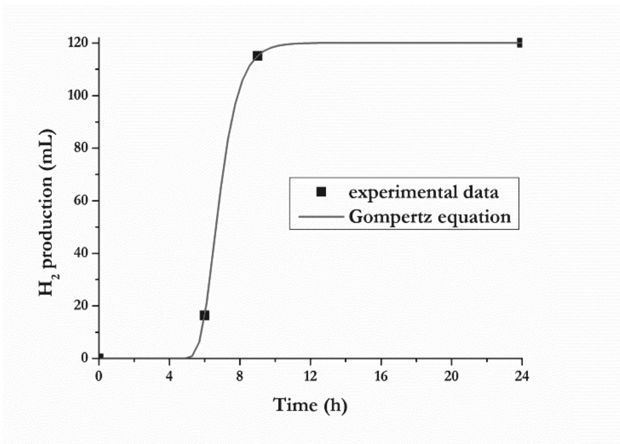

Figure 4. Kinetics of H2 production

wastewater nearly doubled as the HRT increased from the 4th hour to the 12th hour, but the further increase to 16–24 h improved the VFA production only by 6% [27]. In the case of sludge used for VFA production, both the waste substrate and microbial mixed cultures are present in the same phase. Most of the studies found that lower HRT is beneficial to the production of VFA from waste activated sludge [28]. This is because it can prevent the dominance of methanogens in the anaerobic reactor as the growth rate of methanogens is lower than that of acidogens. Nevertheless, the HRT should be sufficiently long to promote hydrolysis of the sludge.

Conclusions

Summarizing the data gained in the presented paper, it can be concluded as follows:

1. The lack of CH_4 in both sets of the experiment is probably an effect of a temperature heat-shock which eliminates methanogenic bacteria from the reaction mixture.
2. Organic wastes added to the samples resulted in a high VFA production rate. The amount of VFA was six times higher there than in the samples containing only the sludge.
3. For VFA generation, the whole 24-hour period of the experiment is crucial, whereas hydrogen is produced the most dynamically up to the 9th hour of the anaerobic reaction.
4. The experiment presented in this paper was a pilot case. It is necessary to continue with similar reactions which will tell us more about the optimal conditions for both VFA and H_2 production process from a cheap waste material.

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