Volatile Fatty Acid Production from Organic Fraction of Municipal Solid Waste Through Anaerobic Acidogenic Digestion

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Abstract

There are numerous studies on two-phase anaerobic digestion of municipal solid waste (MSW) in the literature. Yet, in the majority of these studies, applied organic loading rates (OLR) were relatively low. This study differs from those in the literature in terms of high OLR application and focuses on the optimization of the acidification phase. Effect of high OLRs and pH values were investigated and optimum operational conditions for acidification were determined. Although conversion of particulate organics to soluble chemical oxygen demand (COD) was achieved in the reactors, total COD values remained the same. Various types of organic acids were produced in the reactors and the selective production of organic acids in the anaerobic acidogenesis process was possible by controlling the organic loading rate and pH. Optimum OLR and pH values were determined as 15 g volatile solid (VS)/L·day and 5.5 ± 0.1, respectively, for the MSW composition investigated.

Key words: acidification; anaerobic; organic loading rate; organic fraction of municipal solid waste; pH

Introduction

Organic fraction of municipal solid waste (OFMSW) is semisolid waste that brings about significant environmental and public health problems. These problems include contamination of drinking water supplies, global warming enhancement, and odors (Ostrem, 2004). The total production of municipal solid waste in Turkey was 25 million tones per year for 2004, and only 28% of this waste was disposed in landfills. On the other hand, no engineered waste management practices were applied to the remaining percent, which represents a significant danger to the environment. Various approaches to municipal solid waste (MSW) management problem such as landfilling, composting, incineration exist; however, anaerobic digestion (AD) has advantages over these techniques in terms of process control and efficiency, operation time, and production of value added products, such as biogas, etc.

AD can be operated in single- or two-phase configurations. Single-phase incorporates both acid formation and methane production in the same reactor, whereas a two-phase operation separates acid formation from methane production (Speece, 1996). Two-phase processes have some advantages over one-phase systems. First of all, the selection and enrichment of different bacteria is achieved, and the control of acidification phase enhances the stability of the system by preventing overloads that may affect methanogens. Another advantage is that the volume requirement can be smaller due to applicability of short hydraulic retention times, and therefore, the system is more cost effective. Last, through acidification high solid containing wastes are liquefied, and this increases the efficiency of the system. Furthermore, conventional one-phase digestion is not effective for wastes with high solid content because a significant increase in fluid and digester volume is observed during one-phase operation systems (Demirer and Chen, 2005).

There are numerous studies (Virturtia et al., 1995; Raynal et al., 1998; Vieitez and Ghosh, 1999; Wang et al., 2002; Bouallagui et al., 2004; Gioannis et al., 2008) on anaerobic digestion of MSW with two-phase systems in the literature. Yet, in the majority of these studies, applied organic loading rates (OLRs) were generally lower than 10 g volatile solid (VS)/L·day because they were lab-scale applications (Diaz et al., 1981; Viturtia et al., 1995; Hartmann and Ahring, 2005). In addition, these studies did not focus on the optimum operational conditions for the acidification of OFMSW. However, acidification should be controlled to obtain maximum efficiency in the methane producing reactor in a two-phase system. Therefore, this study differs from the literature in terms of high OLR application and focuses on acidification phase optimization. The effect of high OLRs and pH values was studied and optimum operational conditions for acidification were determined in terms of load and pH value.

Materials and Methods

Organic fraction of MSW and anaerobic seed culture

The OFMSW used in this study was composed of food wastes collected from houses and vegetable and fruit wastes...
Table 1. Typical Solid Waste Composition in Turkey

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile</td>
<td>0.56</td>
</tr>
<tr>
<td>Metal</td>
<td>1.13</td>
</tr>
<tr>
<td>Glass</td>
<td>2.12</td>
</tr>
<tr>
<td>Plastic</td>
<td>2.55</td>
</tr>
<tr>
<td>Paper</td>
<td>6.47</td>
</tr>
<tr>
<td>Organic</td>
<td>64.15</td>
</tr>
<tr>
<td>Others (ash, slag, inert materials)</td>
<td>23.02</td>
</tr>
</tbody>
</table>

Table 2. Operational Conditions of the Reactors

<table>
<thead>
<tr>
<th>Reactor</th>
<th>OLR (g VS/L/day)</th>
<th>HRT (day)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>10</td>
<td>2</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>R2</td>
<td>15</td>
<td>2</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>R3</td>
<td>20</td>
<td>2</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>R4</td>
<td>15</td>
<td>2</td>
<td>6.5 ± 0.1</td>
</tr>
<tr>
<td>R5</td>
<td>15</td>
<td>2</td>
<td>No control</td>
</tr>
</tbody>
</table>

OLR, organic loading rate; VS, volatile solid; HRT, hydraulic retention time.

The mixed anaerobic culture from the anaerobic digesters of Ankara Central Wastewater Treatment Plant was used as inoculum. The volatile suspended solid (VSS) concentration of the sludge was 8017 ± 1438 mg VSS/L. The seed sludge was screened through a 1-mm size sieve before use to remove debris, fibers, etc.

Experimental setup

Five continuously stirred tank reactors (CSTR) were operated during the course of the study. In the first part of the experiments, OLRs of 10, 15, and 20 g VS/L.day were applied to the three CSTR reactors named R1, R2, and R3, respectively. A continuous feeding procedure was not applied; the reactors were fed once in a day. The organic loads were set by the change in the substrate concentration. The pH value of the first three reactors was kept constant at a value of 5.5 ± 0.1 and hydraulic retention time (HRT) was 2 days. After the determination of optimum OLR in the first part, two more reactors, R4 and R5, were operated at this optimum load in the second part with the same HRT value. The pH value of R4 was 6.5 ± 0.1, whereas pH control was not practiced for R5 (Table 2).

The reactors (R1, R2, R3, and R4) were operated as pH-stat CSTRs (Demirer and Speece, 1999). The pH-stat CSTR system consisted of a magnetically stirred glass reactor of 1-L effective volume with a headspace of 500 mL (Fig. 1). The reactor was sealed with a rubber stopper containing ports for pH-probe, NaOH solution addition, feeding, and gas venting. Biomass recycle was not applied in the system. The pH controller was connected to the pH probe and peristaltic pump. When pH value decreased to below the set value of 5.5 ± 0.1 or 6.5 ± 0.1 due to acid production, the controller operated the pump and NaOH solution was delivered to the reactor until the pH value increased again up to 5.5 ± 0.1 or 6.5 ± 0.1. Thus, the pH of the reactors was kept at a constant value.

Analytical methods

Volatile fatty acid (VFA) and ethanol measurements were conducted by using a Trace Gas Chromatograph (GC) Ultra (Thermo Co., Italy) with a Zebron ZB-FFAP column, having length of 30 m, internal diameter of 0.25 mm, film thickness of 0.25 μm, and injector temperature of 250 °C. Helium was the carrier gas in the system. Formic acid (98%, Riedel-de Haen, Germany) was added to the filtered samples to decrease the pH below 3.0 for the conversion of VFAs to their undissociated form. The pH values were measured by pH-meter and pH probe (Hanna Instruments HI 8314 Membrane). The total solid (TS), VS, VSS, total phosphorus (TP), and total Kjeldahl nitrogen (TKN) measurements were performed according to the Standard Methods (American Public Health Association, 2005). The total chemical oxygen demand (tCOD) and soluble (sCOD) analysis were carried out using HACH COD (0–1,500) vials at 150 °C for 2 h, and the COD values were measured by a HACH spectrophotometer. The sCOD of the samples were filtered from 0.45-μm Millipore filter papers before the analysis. The results are depicted in Table 3.

Table 3. Characterization of the Waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>1022.0 ± 8.5</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>963.0 ± 9.2</td>
</tr>
<tr>
<td>Total solids (g/kg)</td>
<td>299.0 ± 6.4</td>
</tr>
<tr>
<td>Volatile solids (g/kg)</td>
<td>262.0 ± 3.7</td>
</tr>
<tr>
<td>Total COD (g/kg)</td>
<td>241.0 ± 2.5</td>
</tr>
<tr>
<td>TKN (g/kg)</td>
<td>4.00 ± 0.50</td>
</tr>
<tr>
<td>Total phosphorus (g/kg)</td>
<td>2.00 ± 0.10</td>
</tr>
<tr>
<td>pH</td>
<td>5.18 ± 0.20</td>
</tr>
</tbody>
</table>

COD, chemical oxygen demand; TKN, total Kjeldahl nitrogen.
Results and Discussion

The influent and effluent tCOD concentrations were very close to each other in all reactors, and it can be concluded there was no removal in tCOD values during the study (data not shown). It is already stated in the literature that there is minimal or no reduction of tCOD in the acid fermentation stage of an anaerobic system because complex compounds such as short-chain fatty acids, alcohols produced, and new bacteria cells exert an oxygen demand (Speece, 1996; Guerrero et al., 1999). As a result, although the conversion of particulate organics to soluble COD was achieved in the reactors, the tCOD values remained the same.

On the other hand, effluent sCOD concentrations increased throughout the operation period due to the hydrolysis of particulate organic matter as stated in the literature (Argelier et al., 1998; Guerrero et al., 1999; Wang et al., 2002) (Fig. 2). In other words, conversion of organic matter into organic acids resulted in increases in sCOD concentrations. As depicted in Fig. 2a, the effluent sCOD concentrations were different in the reactors having the same pH but different organic loads (R1, R2, and R3). The maximum effluent sCOD concentrations were measured as 19,460, 29,800, and 32,588 mg/L in the reactors R1, R2, and R3 with the OLR of 10, 15, and 20 g VS/L.day, respectively. Clearly, the effluent sCOD concentrations increased mainly due to the enhancement of the hydrolysis process resulting from load increase. At the end, more organics in soluble form were formed. In addition, the amount of particulate organic matter in the influent increased as the load increased, which might also bring about a rise in the concentration of the soluble matter during hydrolysis. As a result, R3 had the maximum effluent sCOD concentrations throughout the experiment.

Meanwhile, the pH value of the reactors also affected the effluent sCOD concentrations. An increase in the pH value from 5.5 ± 0.1 to 6.5 ± 0.1 resulted in a decrease in the hydrolysis performance. The solubilization in R2 with pH 5.5 ± 0.1 was higher than in R4 and R5 with pH 6.5 ± 0.1 and

![Fig. 2. Effluent soluble chemical oxygen demand (sCOD) concentrations of reactors at (a) different organic loading rates (OLRs), (b) different pHs.](image-url)
no pH control, respectively; which can also be observed by the highest effluent sCOD of 29,800 mg/L (Fig. 2b). On the other hand, maximum sCOD concentration in R4 was measured as 17,820 mg/L. Moreover, the pH value of R5 dropped to below 4.0, around 3.5 ± 0.1, throughout its operation period. Hence, R5, with its lowest effluent sCOD concentration of 12,470 mg/L, had the minimum solubilization performance due to effect of low pH value on hydrolysis as Bouallagui et al. (2004) explained in their study. The results indicated that pH values higher than 5.5 ± 0.1 and lack of pH control in the reactors affected the acid phase performance adversely; that is, low solubilization efficiency was observed in the reactors. As a result, the optimum pH value was determined as 5.5 ± 0.1 for the highest acidification process, which was also supported by the literature (Yu and Fang, 2002).

The tVFA production indicated similar trends to sCOD variations (Fig. 3a). The variations in tVFA and sCOD were related. That is, the acid production led to rise in sCOD values. R3, the reactor with the maximum organic loading, had the highest acid production during experiments mainly due to the hydrolysis enhancement, and increase in the amount of organic matter in the influent. The average acid concentrations were measured as 8,419, 12,405, and 15,244 mg/L (as acetic acid) in the reactors R1, R2, and R3, respectively. In conclusion, the production of organic acid increased resulting from the load increase applied to the reactors. On the other hand, pH change in the reactors also affected the total acid production results throughout the study. The average values of acid productions were 5,168 mg/L and 1,794 mg/L (as acetic acid) in R4 and R5, respectively. As the results depicted, the minimum production was observed in R5 with its lowest pH value, which clearly indicated the adverse effect of low pH value on microbial metabolism (Yu and Fang, 2003). Moreover, the application of pH 6.5 ± 0.1 did not enhance the acidification process; hence, the acid production in R4 was also lower than that observed in R2 (Fig. 3b).

When the acid compositions were observed, the main species in R1 appeared to be acetic, butyric, caproic, and propionic acids with the percentages of 59, 15, 12, and 7%, respectively. On the other hand, 71% of acetic acid, 8% of

![FIG. 3. Total volatile fatty acid (VFA) concentrations observed in reactors at (a) different OLRs, (b) different pHs.](image-url)
caproic acid, 6% of butyric and propionic acids, and 4% of heptanoic acid were observed in R2 throughout the experiment. Finally, the percentages of VFA measured in R3 were 75, 12, and 6% for acetic, caproic, and butyric acids, respectively (Fig. 4a). The isobutyric, valeric and heptanoic acid percentages were relatively low in all the reactors having the same pH value but different loading rates; namely, R1, R2, and R3 (Fig. 4a). According to the literature (Viturtia et al., 1995; Traverso et al., 2000; Liu et al., 2006), types of organic acids produced as a result of solid waste acidification vary due to the complex nature of this waste. However, the main products were reported to be acetic, butyric, and propionic acids, which were also observed in this study. However, the acetic acid has the maximum concentration in production among other acids because short-chain fatty acids are more likely to be observed in the anaerobic reactors fed by complex substrate like solid wastes (Guerrero et al., 1999).

Furthermore, the effect of pH on the acidification products was investigated in the study. As depicted in Fig. 4b, the rise in pH to the value of 6.5 ± 0.1 resulted in a decrease in acetic acid percentage, whereas the propionic and butyric acids were increased as reported in the literature (Horiuchi et al., 2002). Consequently, although the acetic acid percentage was 58% in R4, the values increased up to 71 and 81% in R2 and R5, respectively. Moreover, the accumulation of propionic acid resulted in low efficiency in the methanogenic phase due to low acidogenic rate of this acid (Wang et al., 2006). Therefore, keeping pH at value of 6.5 ± 0.1 might decrease the efficiency when the propionic acid rise was considered at this pH. On the other hand, low pH value favored the acetic acid production in R5 (Wu and Lin, 2004), yet the remaining acids were relatively low in terms of production percentages. The reason might be the negative effect of low pH value on microbial substrate degradation; that is, acetic acid, with its simple structure, was more likely to be produced by the micro-organisms that were under the stress caused by low pH; however, complex ones were not.

Ethanol, which is classified as one of end-products of anaerobic acidification process of solid waste, is produced mainly due to the glucose fermentation (Batstone et al., 2002). The production of ethanol was also observed in this study, most probably because of glucose in the solid waste used. The maximum ethanol concentrations measured in the reactors were 766, 1,120, and 1,686 mg/L for the R1, R2, and R3, respectively. The increase in load resulted in a rise in the ethanol production for the reactors having same pH value. On the other hand, the effect of pH on the ethanol production was different. The maximum concentration was measured at lowest pH with a value of 1,363 mg/L. The literature studies revealed that ethanol production increased as the pH value

![FIG. 4. Percentages of VFAs observed in reactors at (a) different OLRs, (b) different pHs.](image-url)
dropped below 5.5 (Ren et al., 1997; Rodriguez et al., 2006). On the other hand, R2 and R4 had ethanol concentrations of 1,120 and 1,179 mg/L, respectively. Hence, it can be concluded that there was no significant change in the ethanol concentration when the pH value was shifted from 5.5 ± 0.1 to 6.5 ± 0.1.

Another way of evaluating the acidification performance is the calculation of acidification degree; which is described as the ratio of COD-equivalent of acidogenic products to the total COD (Dinopoulou et al., 1988; Fang and Yu, 2001; Demirel and Yenigun, 2004). The analysis of variance calculated by Student’s t-test was applied for all acidification values to check the reliability of data, that is, to check whether increases or decreases in the degree were really significant or not. At the end, the results showed that the values were 80% different than each other.

The average acidification percentages were estimated as 26 ± 5%, 28 ± 8%, and 23 ± 4% for R1, R2 and R3, respectively (Fig. 5a). The results revealed that the degree increased with an increase in organic load as stated in the literature (Dinopoulou et al., 1988; Raynal et al., 1998; Demirel and Yenigun, 2004). However, further increase resulted in a decrease in the efficiency due to the extra organic load on acidogenic bacteria (Oktem et al., 2006). Furthermore, the high tVFA production might cause inhibition on microorganisms, the result of which might be the inefficiency in the acidification of solid waste (Vieitez and Ghosh, 1999). On the other hand, the percentages in R2, R4, and R5 appeared to be 28 ± 8%, 14 ± 7% and 5 ± 2%, respectively (Fig. 5b). It is clear that the effect of uncontrolled pH value again revealed itself in the system in terms of acidification degree; that is, R5 had the minimum acidification degree with 5 ± 2%. Moreover, increasing pH value from 5.5 ± 0.1 to 6.5 ± 0.1 did not improve the acidification performance and therefore, it can be concluded from the results that the best pH value for the maximum acidification was 5.5 ± 0.1 in this study. Actually, the percent values obtained in this study were not compatible with the ones estimated in the literature. As the percentages varied between 29.7% and 61% in the literature studies (Dinopoulou et al., 1988; Raynal et al., 1998; Guerrero et al., 1999; Fang and Yu, 2001; Bouallagui et al., 2004), the values estimated in this study were lower than the stated ones. The reason may be the higher organic loading rates applied in this study. It is apparent that, the low organic loads were chosen in most of the lab-scale studies, and these low loads were easily degraded by micro-organisms; and

![FIG. 5. Average acidification percentages of the reactors (a) different OLRs, (b) different pHs.](image-url)
clearly high acidification percentages were achieved. However, it should also be noted that a more representative comparison cannot be made during the course of data interpretation because every study has its unique system configuration and operational parameters.

Conclusions
The following conclusion can be drawn based on the results of this study:

1. The maximum increase in the effluent sCOD concentration through hydrolysis was observed at pH 5.5. Although the pH values below 4.0 adversely affected the acidification performance.

2. The selective production of organic acids in anaerobic acidogenesis process was possible by controlling the OLR and pH. OLR increase enhanced the acetic acid production, whereas the butyric acid production decreased with the increase in OLR.

3. pH controlled reactors had higher organic acid productions than uncontrolled one.

4. The maximum VFA production was observed at OLR of 20 g VS/L-day at pH value of 5.5. However, the maximum acidification percentage (28 ± 8%) was observed at an OLR of 15 g VS/L-day.

5. The amount of NaOH added to keep the pH at the desired value at the highest OLR of 20 g VS/L-day made the operational condition unfeasible for large-scale applications in terms of the cost.

6. The optimum operational conditions for the maximum acidification efficiency for the waste composed of food, vegetable, fruit, and paper were determined as OLR of 15 g VS/L-day, pH value of 5.5 and HRT/SRT of 2 days, respectively.

Acknowledgments

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Author Disclosure Statement

The authors declare that no conflicting financial interests exist.

References


