Anaerobic batch digestion of biodegradable plastics

Abstract

Anaerobic batch digestion of some selected biodegradable plastics (BIOPLAs) was studied at 50°C. The BIOPL were Biobas (Novamont starch based resin), oxobag (oxodegradable plastic), PLA straw, PHA yellow bag, LDPE clear bag, PLA cups, Ecoflex (poly tetramethylene adipate-co-terephthalate), and bagasse sugar cane plates. In addition to the BIOPL, Kraft paper was also evaluated. The results showed that, after about 43 days of digestion, the biogas yields were 0.187, 0.104, 0.024, 0.836, 0.061, 0.042 and 0.053 L/gVS of Bio-bag, Oxo-bag, straws, yellow bag, clear plastic, cups, and Ecoflex, respectively.

Introduction

Plastics are very important for many domestic and industrial applications. Shimao (2001) mentioned that the annual world production is about 140 million tones of synthetic polymers. Plastics represented about 12% and 25%, respectively of the total weight and volume of municipal solid waste (MSW) generated in the United States (Franklin Associates Ltd., 1998). Only 5% of the total weight of plastic is recycled. The vast increase in plastics consumption has led to the so called “white pollution”, landfill depletion and threatening of many public works (Ren, 2003). These are due to the high volume to weight ratio and the resistance to degradation. In addition to solving of the aforementioned problems, biodegradable plastics could help to conserve the fossil fuel, and contribute to sustainable development (Ren, 2003).

Biodegradable plastic (BIOPLAS) may be defined as a plastic, derived mainly from renewable raw materials, that its chemical structure and physical properties are changed significantly under the action of naturally established microorganisms such as bacteria, archaea, fungi and algae (Stevens, 2002). Definitions and standards for biodegradable plastics are all based on their compostability (Ren, 2003). He also mentioned that under standard landfill conditions, biodegradable plastics will make no difference from those plastics they have replaced. But, these plastics could be swiftly degraded under controlled composting or anaerobic facilities. Development of standards and specify the conditions for quick degradation of biodegradable plastics are important. There are many factors affecting the biodegradability of polymers. Among them (Zee, 2004):
1- The accessibility of the polymer to enzymatic system;
2- The chemical properties such as the chemical linkage in the polymer backbone, the position and the chemical activity of pendant groups, and the type and the chemical activity of end-groups;
3- The molecular weight distribution of the polymer;
4- Grafting the polymers with other non-biodegradable polymer.
Rivard et al. (1995) mentioned that due to the relatively low costs of landfilling, it will continue to be the major disposal method in the future. Therefore, they mentioned that the anaerobic digestion is the most useful test for examining biodegradability. Ishigaki et al. (2004) studied the degradability of four kinds of commercial biodegradable plastics under aerobic and anaerobic conditions. They mentioned that the biodegradable plastics derived from natural polymers, such as starch or cellulose; contain recalcitrant components to microbial degradation. Results showed that degradation behavior of commercial biodegradable plastics is different from pure polymers due to the additives used to improve the performance of the final product. Selection of an appropriate technology for plastic disposal depends on the kind of plastic (Ishigaki et al., 2004).

Thermophilic anaerobic digestion of the organic fraction of MSW has been successfully applied in lab-scale (Angelidaki et al., 2006) and full scale (Cozzolino et al., 1992). The behavior of BIOPLAS during the digestion of the MSW is not known. Therefore, the main objective of this study was to study the fate of some selected commercial biodegradable plastics under thermophilic anaerobic digestion.

Materials and Methods

2.1. Substrates

Eight commercialized PIOPLAS were examined in this study: Biobas, oxobag, PLA straw, PHA yellow bag, LDPE clear bag, PLA cups, Ecoflex, and bagasse plates. BioBag is made from the Novamont resin, derived from corn starch, in combination with fully biodegradable aliphatic polyesters, aliphatic/aromatic polyesters or in particular polylactic acid (ExcelPlas Australia, 2003). Ecoflex is a statistical aliphatic-aromatic copolyester based on 1,4-butanediol and the dicarboxic acids, adipic acid and terephthalic acid (ExcelPlas Australia, 2003). Its proper name is poly tetramethylene adipate-co-terephthalate. Biogas production from these eight substrates was compared with that produced from Kraft paper. These substrates were codigested with food waste for two reasons. Firstly, the non-recycled plastics generally are present in MSW that contains food waste and secondly, food waste was added a source for macro and micro elements necessary for microorganisms’ growth.

2.2. Inoculum

Two experimental runs were carried out. In the first run, reactors were inoculated with 100 ml of digested food waste which was obtained from lab scale batch thermophilic reactors. The Total solids (TS) and volatile solids (VS) of the sludge were 18.56 and 9.78 g/L, respectively. In the second run, the reactors were inoculated with 200 ml of the effluent of the first run. The TS and VS contents of that inoculum were 2.3 and 1.13 g/L, respectively.
2.3. Reactors start-up

In both experimental runs, reactors each with a total volume of 1000 mL were used in this study. The digestion tests were performed at an initial loading of 4gVS/L: 2 gVS/L of food waste and 2 gVS/L from each plastic type. At the beginning of the experiments inoculum was added. Then the required amounts of substrates were added to each reactor and then the reactors were filled to an effective volume of 500mL with tap water. Then rubber septum and a screw cap were placed to seal each reactor. To assure anaerobic conditions, each reactor was purged with helium gas for 5 minutes. Two reactors contained 2 gVS/L food waste, 200 ml of inoculum and tape water were used as a control to correct the biogas produced from food waste and inoculum. All experiments were performed in duplicate under thermophilic conditions 50 ±1 °C. After one week the reactors contained plates and paper were inhibited as compared with others. Therefore, the reactors of these two substrates were similarly started again but using 1 gVS/L of food waste and 2 gVS/L from each substrate. The average initial pH of all reactors was 7.4.

2.4. Measurements

2.4.1. Total solids (TS), and volatile solids (VS)

Total solid and volatile solids of the sludge and food waste were measured according to the standard methods (APHA, 1998). The total solids of plastics were also measured according to the same standard methods. Due to the problem encountered in the VS measurements of plastics by APHA (1998), the volatile solids of plastics were measured according to D5630-06 method (ASTM, 2001). In this procedure samples were flamed over a burner before ashed in a muffle furnace at 550°C.

2.4.2. Biogas volume measurements

Each day, pressure was measured in each of the batch reactors headspace using a WAL-BMP-Test system pressure gauge. The biogas in the reactors headspace was released under water to prevent any gas exchange between the reactor and the air. Pressure was then measured a second time to provide the initial conditions for the next day’s test. To determine the biogas volumes of each reactor, the following equation was used:

\[ V_{\text{Biogas}} = \frac{P \cdot V_{\text{head}} \cdot C}{R \cdot T} \]

Where:
- \( V_{\text{Biogas}} \) = daily biogas volume (L),
- \( P \) = absolute pressure difference (mbar),
- \( V_{\text{head}} \) = volume of the head space (L),
- \( C \) = molar volume (22.41 L mol\(^{-1}\)),
- \( R \) = universal gas constant (83.14 L.mbar.K\(^{-1}\).mol\(^{-1}\)),
- \( T \) = absolute temperature (K).
2.4.3. Biogas composition

Methane and carbon dioxide contents of the biogas produced in each reactor was periodically measured using gas chromatography (HP 5890 A). A 1.8 × 0.32 mm Alltech carbospher column was used. Helium was the carrier gas at a flow rate of 60 ml/min. The temperatures of oven and thermal conductivity detector were 100 and 120 °C, respectively. The gas flowed into a helium filled column where a thermal conductivity detector measured the amount of methane, and carbon dioxide in the sample. A gas standard with 60% methane and 40% carbon dioxide was used to calibrate the reactors.

3. Results and discussion

3.1 Characteristics of substrates

The total solids and volatile solids contents of the substrates and sludge are shown in Table 1. The oxobag did not show any loss of organic matter after being heated at 105°C for 24 hours. The total solids of yellow bag had 100 percent VS.

Table 1. Characteristics of the substrates and sludge. Number between parentheses are standard deviations

<table>
<thead>
<tr>
<th>Material Type</th>
<th>TS (%)</th>
<th>VS/TS (%)</th>
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<tbody>
<tr>
<td>Bio-bag</td>
<td>93.48 (0.21)</td>
<td>99.58 (0.12)</td>
</tr>
<tr>
<td>Oxo-bag</td>
<td>100 (0.27)</td>
<td>96.18 (0.03)</td>
</tr>
<tr>
<td>Straws</td>
<td>99.59 (0.01)</td>
<td>94.90 (0.02)</td>
</tr>
<tr>
<td>Yellow bag</td>
<td>99.03 (0.09)</td>
<td>100 (0.02)</td>
</tr>
<tr>
<td>Clear plastic</td>
<td>97.75 (3.13)</td>
<td>99.91 (0.23)</td>
</tr>
<tr>
<td>Cups</td>
<td>99.60 (0.01)</td>
<td>99.98 (0.02)</td>
</tr>
<tr>
<td>Ecoflex</td>
<td>99.96 (0.01)</td>
<td>90.57 (0.48)</td>
</tr>
<tr>
<td>Plate</td>
<td>94.21 (0.14)</td>
<td>99.43 (0.01)</td>
</tr>
<tr>
<td>Kraft paper</td>
<td>96.64 (0.07)</td>
<td>95.72 (0.03)</td>
</tr>
<tr>
<td>Food waste</td>
<td>19.17 (0.42)</td>
<td>92.83 (0.12)</td>
</tr>
<tr>
<td>Sludge</td>
<td>0.24 (0.00)</td>
<td>47.59 (0.35)</td>
</tr>
</tbody>
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3.2 Biogas production from Biodegradable plastics

Figure 1 shows the accumulative biogas production from the digesters treating different plastics at an initial loading of 4 gVS/L (2 g VS of plastics and 2 gVS of food waste) and food waste at an initial loading of 2 gVS/L. Since each reactor was done in duplicates, the average of the two reactors is reported. As can be seen, for food waste and all BIOPLS except yellow bag, that biogas production increased till day 15, then a little biogas was produced. Biogas was produced directly after incubation. From day 3 to day 7, there was a relatively low biogas production rate at about 0.05 L/L.day (data not
shown). Then biogas increased sharply. Except yellow bag, there was a little difference between the BIOPLS and food waste. The biogas yields at the end of the digestion time, after 43 days, from BIOPLAS alone was calculated as the difference between the biogas produced from reactors treating food waste and BIOPLS and that treating food waste alone. The results are shown in Fig. 2. As can be noticed, the biogas yields were 0.187, 0.104, 0.024, 0.836, 0.061, 0.00 and 0.053 L/gVS of Bio-bag, Oxo-bag, straws, Yellow bag, clear plastic, cups, and Ecoflex, respectively. The average final pH were 6.72, 6.74, 6.77, 6.33, 6.77, 6.82, 6.73, 6.87, respectively for Bio-bag, Oxo-bag, Straws, Yellow bag, Clear plastic, Cups, Ecoflex, and food waste.

**Fig. 1.** Cumulative biogas production from the different reactors contained 2 gVS/L of food waste and 2g VS/L of BIOPLS

**Fig. 2.** Biogas yield from different feedstocks at the end of the digestion time
Methane contents of the biogas produced are shown in Fig. 3. As can be seen, for all BIOPLAS reactors, except yellow bag, the methane content increased over the digestion time from about 25% on the first week reaching about 65%-70% at the end of the second week and was almost constant till the biogas production was ceased. The methane contents were almost the same as that obtained from food waste. For the reactor contained yellow bag, the methane content increased also reaching the same level of 65% at the end of the second week then slightly decreased to about 60%. Unlike other reactors, the methane content of the biogas produced from the reactors contained food waste and yellow bag was lower than the values measured for food waste reactors. This reduction in methane content may indicate that the digestion of yellow bag started after the depletion of food waste. This also may be confirmed from that data shown in Fig. 1. As can be noticed from Fig. 1 that the cumulative biogas for all BIOPLAS was almost the same during the first two weeks of digestion then differences were evident.

![Methane contents of biogas production from reactors contained 2 gVS/L of food waste and 2g VS/L BIOPLAS](image)

Fig.3. Methane contents of biogas production from reactors contained 2 gVS/L of food waste and 2g VS/L BIOPLAS

3.3 Biogas production from plates and Kraft paper

The cumulative biogas production from plates, Kraft paper is shown in Fig. 4 together with food waste. The reactors of plates and Kraft paper started with the same amount of sludge and adding 2 gVS of plates or Kraft paper per litter and 1 g VS of food waste was added. Control reactors contained 1 gVS/L of food waste were also incubated to subtract the biogas produced from food waste and inoculum. Similar to the BIOPLAS reactors, biogas started directly after incubation. The biogas production increased till day 15 for food waste and Kraft paper then leveled off. While for the digesters contained
plates, biogas was still increasing till about day 33. The biogas yields from Kraft paper and plates after excluding the cumulative biogas from food waste were 0.133 and 0.507 L/g VS, respectively as shown in Fig. 2. Biogas production rates are shown in fig. 5. As can be depicted that there was a decreased biogas production rate from days 3 to 6. Then there was a peak of biogas production rate at the end of the first week for both Kraft paper and plates. Then the biogas production rates decreased sharply after that. The average final pH was 6.73, 6.84 and 6.98 for plates, Kraft paper, and food waste, respectively.

![Biogas Production](image)

Fig.4. Cumulative biogas production from Kraft paper, plates and food waste using 1 gVS/L of food waste and 2g VS/L of other substrates
Fig. 5. Biogas production rates from Kraft paper, plates and food waste using 1 gVS/L of food waste and 2g VS/L of other substrates

The methane contents of the biogas produced from plates and Kraft paper are shown in Fig. 6. For all reactors, methane contents increased over the digestion time till about day 12 then leveled off. Like the reactor contained both food waste and BIOPLAS, the methane content of the biogas produced from the reactors contained plates and paper was lower than that obtained from food waste reactors. Comparing the data in Figs. 3 and 6 for food waste, it can be seen that the lower initial loading of food waste the higher methane content. This may be due to the lower F/M ratio at lower initial loading of food waste.
Conclusions

References


http://www.epa.gov/garbage/pubs/msw97rpt.pdf


