Co-pyrolysis of Biomass and Cattle Manure to Produce Upgraded Bio-oil

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Abstract—Too low of pH value in bio-oil not only leads to a low quality of bio-oil, but also many problems to its applications. One of the possible upgrading of bio-oil that has been studied is co-pyrolysis. In this work, the bio-oil with low pH value was upgraded by using co-pyrolysis method. Effect of reaction temperature and effect of composition of biomass mixtures on the product yields were studied. The corncob, cattle manure, and corncob/cattle manure mixtures (3:1, 1:1, and 1:3 w/w) were subjected to a pyrolysis process to produce bio-oil. Pyrolysis of temperature range between 350 and 450°C were investigated. The results showed that the individual corncob gave the highest bio-oil yield at 400°C, the individual cattle manure gave the highest bio-oil yield at 450°C and the corncob/cattle manure ratio of 1:3 pyrolysed at the temperature of 400°C showed the best synergistic effect. In addition the individual cattle manure bio-oil has pH value higher than that of the individual corncob bio-oil and the pH value of the corncob/cattle manure mixture bio-oil increases while increasing the cattle manure composition in the corncob/cattle manure mixture. The results indicated that co-pyrolysis of corncob/cattle manure mixture can improve the pH value of bio-oil.

Keywords—Co-pyrolysis, Bio-oil, Corncob, Cattle manure.

I. INTRODUCTION

Currently, the increasing use of fossil fuels for energy production is a matter of concern, both with regards to possible effects on the global climate from the increase in atmospheric carbon dioxide, and in a long-term perspective because the resources are limited. The use of biomass as an energy source is an issue of great importance, as it constitutes part of an alternative solution for the replacement of fossil fuels [1]. Biomass can be transformed into liquid fuel via pyrolysis that occurs in the absence of oxygen to convert biomass into liquid bio-oils together with permanent gases and solid char. Bio-oil can be used in many applications. However, bio-oil has deleterious properties such as high viscosity, thermal instability, corrosiveness, and chemical complexity, which set up many obstacles to its applications [2, 3]. The co-pyrolysis of biomass with animal manure could potentially be a good solution to improve the bio-oil quality. The high nitrogen content of animal manure and low pH of pyrolytic bio-oils may be mitigated if biomass and animal manure are mixed together before being subjected to pyrolysis.

The objectives of this work were to produce bio-oil with higher pH value by co-pyrolysis of biomass with animal manure and to study the effects of temperature and ratio of biomass to manure on the product yields.

II. EXPERIMENTAL

A. Materials

The biomass samples used in this study were corncob and cattle manure. They were air dried at ambient conditions for 24 hours then dried again in an oven at 105°C for 24 hours. Finally the samples were cut into small particles (0.5-3 mm) by wood chipper. The corncob and cattle manure were mixed in a beaker thoroughly by a stirrer in the following ratios: 3:1, 1:1, and 1:3 w/w.

B. Pyrolysis/Co-pyrolysis

The pyrolysis/co-pyrolysis of corncob, cattle manure, and corncob/cattle manure mixtures were carried out in a fixed bed reactor. Fig. 1 shows a schematic diagram of the pyrolysis apparatus that was used. In this study, 700 mL of 316 stainless steel pyrolysis reactor was heated by an electrical furnace. The temperature of the experimental system was adjusted by using a PID temperature controller and was monitored by using a K-type thermocouple. First of all, 400 g of corncob (180 g for cattle manure) were placed in the pyrolysis reactor and the temperature was raised at a rate of 2.5°C/min to the final temperature. After the temperature was reached, approximately 5-10 mg. Experimental runs are carried out using a purge gas flow (100 mL/min) of pure nitrogen and a constant heating rate of 10°C/min is used in all experimental runs, from room temperature to 800°C.

C. Thermogravimetric analysis

Thermogravimetric analysis was carried out in a thermogravimetric analyzer (TGA) model SDT 2960 PN 925605.001, Perkin Elmer. The amount of sample was approximately 5-10 mg. Experimental runs are carried out using a purge gas flow (100 mL/min) of pure nitrogen and a constant heating rate of 10°C/min is used in all experimental runs, from room temperature to 800°C.
Valve, the DTG plot for cattle manure exhibits only one peak of mixture, two peaks occurred between 220 and 360 min stabilization of the mechanically stirred oil.

-Derivative thermogravimetric (DTG) curves of corncob, cattle manure and corncob/cattle manure mixture which are 5.6, 10.7, and 10.5 wt%, respectively. It can be seen that the corncob sample has the lowest moisture content since the result shows the lowest weight loss.

III. RESULTS AND DISCUSSION

A. Thermogravimetric analysis

Fig. 2 shows the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of corncob, cattle manure and their mixture (1:1 weight ratio). In general, three distinct weight loss stages could be identified [4, 5]. The first stage, corresponding to the reduction in mass at temperatures lower than 105°C, attributed to the demoisturization of corncob, cattle manure and corncob/manure mixture which are 5.6, 10.7, and 10.5 wt%, respectively. It can be seen that the corncob sample has the lowest moisture content since the result shows the lowest weight loss.

The second stage, the decomposition temperature of cattle manure and the mixture, started around 210°C while that of the corncob started at 220°C. The DTG plot for corncob between 200 and 360°C showed two observable peaks. The first peak was between 200 and 300°C with maximum peak at 270°C and was lower in height than the second peak. The second peak was between 310 and 360°C with maximum peak at 340°C. The weight loss of corncob cob at the temperatures of 270 and 340°C were 18.5 and 54.2 wt%, respectively. Based on the literature data [6], it was reported that the first DTG peak of the second stage was associated with the decomposition of hemicellulose and cellulose and the second one mainly with decomposition of lignin and of residual charcoal from cellulose and hemicellulose. Unlike the corncob, the DTG plot for cattle manure exhibits only one peak. This peak was between 210 and 360°C with the maximum peak at 310°C. The weight loss of cattle manure at the temperature of 310°C was 32 wt%. It is also noted that this peak might be corresponded mainly to the degradation of cellulose, hemicelluloses and protein [7, 8]. For the DTG plot of mixture, two peaks occurred between 220 and 360°C. The first peak was between 220 and 300°C with the maximum peak at 280°C. And the second peak was between 310 and 360°C with the maximum peak at 340°C. The weight loss of the mixture at the temperatures of 280 and 340°C were 26.2 and 54.0 wt%, respectively. This DTG curve was between DTG of corncob plot and DTG of cattle manure plot.

The third stage, temperature more than 370 to 800°C, weight loss of corncob, cattle manure, and their mixture were lower than the second stage. This stage was to decompose heavier organic compound. At 400°C the pure corncob and the pure cattle manure were decomposed around 66.8 and 49.3 wt%, respectively. If the corncob and cattle manure mixture (1:1 w/w) has no synergy weight loss of the mixture equals sum of the half pure corncob and the half pure cattle manure which is 58.1 wt%. However, in experiment weight loss of the mixture was 63.8 wt% which was higher than sum of the half pure corncob and the half pure cattle manure. It can be concluded that the decomposition of corncob and manure mixture has synergy. At the end of this stage (800°C), the residues of corncob, cattle manure and the mixture were 23.2, 28.6, and 25.1 wt%, respectively.

B. Influence of temperature on product yields

1. Corncob

Operating temperature is one of the most important factors in the pyrolysis process. The effect of temperature on product yields in the pyrolysis of corncob is shown in Fig. 3. Pyrolysis experiments were performed at 350, 400, and 450°C under a nitrogen gas flow rate of 200 cm³/min. As the temperature increased from 350 to 450°C, the gaseous product yields increased from 18.1 to 22.1 wt%, however, the liquid (bio-oil) yields increased from 350 to 400°C and then decreased a little at 450°C. The maximum bio-oil yield of 48.0 wt% was obtained at 400°C. The char yields decreased from 35.6 to 30.0% with the increasing pyrolysis temperature from 350 to 400°C. This may be due to the greater primary decomposition of corncob at high temperatures or through secondary decomposition of the solid residue [9].

The above results are consistent with studies reported in the literatures [5, 10]. Cao et al. [10] studied the effect of temperature on the pyrolysis products of corncob and reported a similar decrease in the char yield, an increase in
the gaseous and liquid product yields with the increasing temperature.

C. Influence of mixture composition on product yields

The influence of corn cob/cattle manure composition on the co-pyrolysis product yields was investigated at 400°C for corn cob/cattle manure ratios of 3:1, 1:1, and 1:3 w/w as shown in Fig. 5. It can be seen that an increase in corn cob content of the mixture increases the bio-oil yield. The bio-oil yield increased from 36.0 to 42.0 wt% when the ratio of corn cob was increased from 1:3 to 3:1. The gas yields were determined by difference and ranged from 16.9 to 22.6 wt% depending on the composition of the mixture. The char yield at the ratios of 1:3 and 3:1 were 47.1 and 35.3 wt%, respectively. It can be seen that char yield decreased with increasing corn cob content. The maximum liquid yield of the mixture was 42.0 wt% for the corn cob/cattle manure mixture at the ratio of 3:1.

2. Cattle manure

The effect of temperature on product yields of cattle manure is shown in Fig. 4. As can be seen, the liquid yield increased from 25.5 to 29.2 wt% when the final pyrolysis temperature was raised from 350 to 450°C. And the maximum liquid yield of 29.2 wt% was lower than that of corn cob. The gaseous yields also increased as the pyrolysis temperature was raised because of the secondary reaction of pyrolysis vapor such as dehydration and gasification [11, 12]. The char yields decreased with increasing temperature due to a greater primary decomposition of cattle manure at high temperatures or through secondary decomposition of the solid residue [9].

The conclusion was consistent with data reported by Xiu et al. [13]. Xiu et al. [13] studied the effect of operating parameters on product yields and characterization of bio-oil for swine manure in hydrothermal pyrolysis process.

The maximum bio-oil yield of 42.0 wt% was obtained at the ratio of 3:1, therefore this ratio was chosen to investigate the effect of temperature on the product yields as shown in Fig. 6. It was evident that the influence of temperature had no significant effect on the product yields. The bio-oil yield was 42.0 wt% at 400°C while it was 42.8 wt% at 450°C. The temperature was increased by 50°C but the amount of bio-oil increased only by 0.8 wt%. High cost was used to raise the temperature from 400 to 450°C and it’s not worthwhile. So the pyrolysis temperature at 400°C was the best choice for use in pyrolysis corn cob/cattle manure mixtures.

The product yields of the mixtures from calculation (from pyrolysis of each part separately) compared with the product yields of the mixtures from experiment are shown in Fig. 7. The amount of char products (from calculation) from co-pyrolysis of the mixtures of corn cob and manure at the ratios of 3:1, 1:1, and 1:3 were 38.5, 44.3, and 50.1 wt%, respectively. But the actual yields of char (from experiment) were 35.6, 40.7, and 47.1 wt%, respectively. It can be seen that char yields from calculation were higher than those from experiment. So it can be said that char yield decreased when corn cob was mixed with cattle manure. The bio-oil yields of mixtures (from calculation) at the ratios of 3:1, 1:1, and 1:3 were 42.8, 37.6, and 32.4 wt%, respectively. But the actual yields of bio-oil (from experiment) were 42.0, 39.4, and 36.0
wt%, respectively. And the gaseous yields of mixtures (from calculation) at the ratios of 3:1, 1:1, and 1:3 were 18.7, 18.1, and 17.5 wt%, respectively. The actual yields of gaseous (from experiment) were 22.6, 20.0, and 17.0 wt%, respectively.

Fig. 6 Dependence of the product yields of corncob/cattle manure at the ratio of 3:1 on pyrolysis temperature.

These results demonstrated that cattle manure affected product yields and its effect depended on composition of the mixture.

The percentage of synergistic effect =
\[
\frac{\text{Product yield from experiment} - \text{Product yield from calculation}}{\text{Product yield from calculation}} \times 100
\]

Fig. 8 Synergistic effect of product yields.

D. pH of bio-oils

The pH values of bio-oils produced from different ratios of cattle manure and corncob at a fixed operating temperature of 400°C are shown in Table I. Basically, the mixtures were compared with pure (100 wt%) cattle manure and pure corncob in order to understand the effect of cattle manure in corncob. From this table, it was seen that the pH values of the bio-oil increase while increasing the content of cattle manure. The pH values of corncob/cattle manure mixture at the ratios of 3:1 1:1 and 1:3 were 3.16, 3.42 and 3.71, respectively while the pH values of pure cattle manure and pure corncob were 4.63 and 1.95, respectively. The pH values of their mixtures increased with increasing cattle manure content. Since cattle manure has high protein (higher nitrogen content compared with the pure corncob), pyrolysis of cattle manure (nitrogenous compounds with high base) makes high pH value in bio-oil. It can be concluded that adding cattle manure can improve the pH value of bio-oil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Corncob/Cattle manure bio-oils</th>
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<tbody>
<tr>
<td>pH</td>
<td>1.95  3.16  3.42  3.71  4.63</td>
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TABLE I

Summary of pH values of corncob/cattle manure bio-oils.

The percentage of synergistic effect was calculated from (1) to show the effect of cattle manure on product yields as shown in Fig. 8. The percentages of synergistic effects of gas, bio-oil and char products were 20.8, -1.7, and -7.6%, respectively for the co-pyrolysis of the mixtures of corncob and manure at the ratio of 3:1. At the ratio of 1:1 the percentages of synergistic effects of gas, bio-oil and char products were 10.2, 4.7, and -8.2%, respectively. And at the ratio of 1:3 the percentages of synergistic effects of gas, bio-oil and char products were -3.1, 10.9, and -6.0%, respectively. It can be seen that the ratio of 1:3 showed the highest positive synergy for bio-oil yield and negative synergies for char and gas yield and considered the best ratio.

The percentage of synergistic effect =
\[
\frac{\text{Product yield from experiment} - \text{Product yield from calculation}}{\text{Product yield from calculation}} \times 100
\]

Fig. 7 Product yields of the mixtures from calculation compared with product yields of the mixtures from experiment. E = experiment, C = calculation.

As the conclusion of this work, TGA of corncob, cattle manure, and their mixture (1:1) suggests that the decomposition start around 200°C and the synergistic decomposition effect of the co-pyrolysis was observed. Co-pyrolysis of corncob and cattle manure at the ratios of 3:1, 1:1, and 1:3 by wt, the best synergistic effect was found in the ratio of 1:3 for the highest positive synergy of bio-oil yield and
negative synergies of char and gas yields. Moreover, the bio-oil yields increased with an increase in corncob content.

In addition, the pH of bio-oils increased when cattle manure content increased. It showed that co-pyrolysis of corncob with cattle manure can improve pH of bio-oils. In this study the ratio of 1:3 gave the highest pH value of 3.71.

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REFERENCES


