Yield and Composition of Bio-oil from Co-Pyrolysis of Corn Cobs and Plastic Waste of HDPE in a Fixed Bed Reactor

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Pyrolysis, a thermal cracking process in inert environment, may be used to produce bio-oil from biomass and plastic waste by pyrolyzing the biomass and plastic materials in one fixed bed reactor to take advantage of plastic pyrolysis which produces non-oxygenate components needed for bio-fuel manufacture. Corn cobs as biomass waste and high density polyethylene (HDPE) plastics were used as feeds in the pyrolysis. Corn cobs were considered due to their high abundant waste and high combined cellulose and hemicellulose content (about 84%), which is favourable to produce high yield of bio-oil. HDPE waste was selected with consideration that their waste tonnage is very high and has not been properly treated as non-biogradable waste. In co-pyrolysis of plastic and biomass wastes, degradation of plastic reduces oxygen content and increases carbon content, therefore increasing bio-oil heating value.

In case of slow pyrolysis of different types of biomass residence time needed is 450-550 seconds for heating rate of 6-60 °C/minute in which longer residence time is required for lower heating rate. Co-pyrolysis of HDPE and waste oil at different temperatures between 300 to 600 °C, residence time required is 2-8 seconds. Almost all co-pyrolysis of biomass and plastic exhibit residence time in the order of seconds. Therefore, to allow contribution of plastic
pyrolysis to the bio-oil content, conditions of co-pyrolysis should be controlled by conditions of plastic pyrolysis. High flow of inert gas $\text{N}_2$ has been applied in the present work to shorten the residence time of pyrolysis to avoid secondary pyrolysis of plastic material and obtain more oil. Most of pyrolysis of biomass use fast pyrolysis (heating rates of 10-200 K/second) to obtain high yield of bio-oil. Under this condition, yield of bio-oil could reach 60-75% with 15-25% of solids and 10-20% of gaseous phase depending on the type of biomass feed used. The use of slow pyrolysis (heating rates of 0.1-1 K/second) makes vapour residence time too high (5 to 30 minutes) where components in vapour phase react each other to form solid char and other liquids which could adversely reduce the yield of bio-oil.

On the other hands, most of pyrolysis of plastics undergoes relatively low heating rates (slow pyrolysis) in order to obtain high yield of oil product.

Some workers investigating co-pyrolysis of biomass and plastics in general use low heating rate pyrolysis kept at 5 °C or 10 °C/minute (slow pyrolysis) to obtain high yield of oil. It appears that plastic pyrolysis controls the production of bio-oil in co-pyrolysis. One of advantages of slow pyrolysis is to allow adjustment of residence time of gas to determine yields of pyrolysis. Using slow pyrolysis in biomass pyrolysis with longer residence time of gas in the reactor, lower molecular weight will be increased. Shorter residence time in seconds is required to suppress secondary pyrolysis and enhance yield of oil. Using fast pyrolysis (heating rate>300 °C/minute) control of residence time is more difficult.

Previous studies show that combining plastic to the pyrolysis of biomass will yield more oil with higher heating value due to contribution of plastic hydrocarbons in the forms of paraffins, isoparaffins, olefins, naphthenes and aromatics. Method of co-pyrolysis is more desired to produce pyrolysis oil than mixing of oil from biomass pyrolysis and that from plastic pyrolysis. Interaction of radicals during co-pyrolysis reactions can avoid the phase separation if the mixing had been carried out thus improving stability of pyrolysis oil. Oral observed that some radical reactions in co-pyrolysis proceed through steps of initiation, formation of secondary radicals through depolymerisation, formation of monomers, reactions of hydrogen displacement (formations of paraffins and dienes), isomerisation through vinyl functional groups, and eventually termination by disproportionation and radical recombination.

The pyrolysis of corn cobs has been carried out by some workers. All these works show that none of the workers have investigated co-pyrolysis of corn cobs and plastics. The present research proposes co-pyrolysis of corn cobs and plastic material HDPE using co-pyrolysis at low heating rate. The work by Paradela shows that co-pyrolysis increases short carbon chain paraffin content in bio-oil similar to component content in bio-fuel. Therefore, the addition of plastic is expected to reduce oxygenate content in bio-oil thus increasing its heating value.

Polyethylene is one of thermoplastic types abundantly used in daily life. Polyethylene is white with melting point 110-117 °C and molecular weight 50,000-30,000. Some types of polyethylene are Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Linear Low Density Polyethylene (LLDPE). HDPE has straight chain structures, LDPE has branched chain structure with short or long branches, while LLDPE has straight polymer chains with short branches. Density of HDPE is higher than that of LDPE, in which HDPE’s density reaches 0.95 g/cm³ while LDPE’s 0.915-0.925 g/cm³.

This research is aimed at evaluating effect of mass composition of HDPE material in the feed blend of co-pyrolysis of corn cobs and HDPE on bio-oil yield and chemical composition of bio-oil product. The conversion of bio-oil containing oxygenates to bio-fuel is usually carried out by deoxygenation and followed by hydrocracking. Olefins resulting from pyrolysis of plastics may be hydrogenised to convert to paraffins as main components in bio-fuel.

2. Experimental

Corn cobs as biomass feed to the pyrolysis were prepared by drying in an oven at 105 °C to reach moisture content of 10%. Dry corn cobs then were crushed and sieved to obtain particles with sizes 2-4 mm. The results of ultimate and proximate analysis are shown in Table 1. The table shows that moisture contents in biomass and

<table>
<thead>
<tr>
<th>% weight</th>
<th>HDPE</th>
<th>Corn cobs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>15.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Ash</td>
<td>0.08</td>
<td>1.56</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>84.90</td>
<td>70.12</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>0.02</td>
<td>18.32</td>
</tr>
<tr>
<td>Carbon</td>
<td>84.74</td>
<td>46.58</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>11.95</td>
<td>5.87</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.02</td>
<td>0.47</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.66</td>
<td>0.04</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.63</td>
<td>45.46</td>
</tr>
<tr>
<td>H/C mole ratio</td>
<td>1.69</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table 1. Results of proximate and ultimate analysis of corn cob and HDPE particles
HDPE plastic materials were low, i.e. 10 and 15% weight, respectively. The presence of high moisture can increase the load of the heating and it may impure the bio-oil. Therefore, its content is restricted to favour processing bio-oil if it would be converted to bio-fuel.

High content of oxygen in corn cobs (nearly half of the weight) is expected to evolve as oxygenates in the pyrolysis products, which are not desirable because they are attributed to low heating value of the bio-oil. On the other hands, low content of oxygen and high carbon content in HDPE material gives favourable contribution to high heating value of the bio-oil. Therefore, blending of both corn cob and plastic material as feeds of the pyrolysis was expected to improve the heating value of bio-oil produced by corn cob pyrolysis.

Volatile matter was determined in accordance with ASTM standard number 3175 in which approximately 2 g of the biomass or plastic material with particle size 425 μm was placed in a porcelain crucible, oven-dried, kept in a furnace at a temperature of 550°C for 10 min and weighed after cooling in a desiccator. This method has been adopted from the measurement of volatile matter content in coal particles. The reduction of the weight is the measure of amount of volatile matter resulting from the drying. This amount is a rough measure how much the material is cracked during the pyrolysis. Higher volatile matter biomass at appropriate conditions is expected to produce higher bio-oil yield. High volatile matter measured upon corn cob particles was expected to produce large amount of bio-oil. Fixed carbon content can be considered as a rough measure how much char remains in the pyrolysis reactor when the pyrolysis ends. Low fix carbon measured upon HDPE plastics was expected to produce small residue after the pyrolysis ends.

Ash content affects the capability of external heating in the pyrolysis reactor on the heating of the pyrolysis feed because it can absorb the heat which actually is used to heat up the feed of the pyrolysis. Additionally, high ash content composing mostly alkali compounds contributes to the reduction of oil yield. It seems that alkali compounds have high heat capacity which can absorb heat convected to the pyrolysis feed. Very low ash content has been obtained from the proximate analysis both in plastic and biomass materials and expectedly did not affect the heating of the pyrolysis feed.

Pyrolysis was conducted in a stainless steel cylindrical reactor with diameter and length 60 mm and 250 mm. Feed composing corn cob and plastic particles was located in a boat made of half cylinder sizing 110 mm length and 50 mm diameter. The boat was put horizontally inside the reactor, which was also positioned horizontally. Front end of the boat was connected to a half cone to allow smooth flow of gas N₂ over the outer wall of the boat thus improving convective heat transfer from hot gas to the surface of the boat. The flow of gas N₂ was selected to fulfil maximum residence time of 7 seconds of the pyrolysis gas to avoid secondary reactions of plastic vapour. The feed of about 20 grams for each experiment run was used. The mass ratio of plastic to biomass was varied (0:100, 25:75, 50:50, 75:25, and 100:0) for blend of corn cob and HDPE particles.

Gas N₂ was flowed to the reactor with flow rate of 750 ml/minute. The heating rate of the pyrolysis was set at 50°C/minute to heat gas N₂ from ambient temperature to 500 °C. Hold time was set for 30 minutes for each run to allow more yield of bio-oil. Vapour produced by the pyrolysis reactor was delivered to a condenser using cooling water of about 10°C to condense the vapour and obtain bio-oil. This oil was dropped into an Erlenmeyer flask with uncondensed vapour disposed to ambient.

Bio-oil collected in the flask was then characterized by GC-MS to identify components in the oil. Other measurements were viscosity and pH of the oil. The yields of oil product were also quantified in order to correlate between composition of plastics and biomass in the reactor feed and yield of bio-oil.

3. Results and Discussion

3.1 Effect of plastic composition in feed blend on bio-oil yield

Table 2 shows that for the pyrolysis involving only plastics (blend type A5), most of plastic material was cracked to form non-condensable gas and only small part became liquid yield. In case of pyrolysis using pure biomass and plastics, increasing flow rate of N₂ from 750 ml/minute to 1400 ml/minute in the present work, which is equivalent to maximum residence time of about 5 seconds, it was found that at N₂ flow rates of 1400ml/min in comparison

<table>
<thead>
<tr>
<th>feed blend type</th>
<th>plastic content in feed blend</th>
<th>yield (% weight)</th>
<th>solid</th>
<th>liquid (bio-oil)</th>
<th>non-condensable gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0</td>
<td>46.10</td>
<td>28.05</td>
<td>25.85</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>10</td>
<td>48.05</td>
<td>25.45</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>25</td>
<td>49.80</td>
<td>21.55</td>
<td>28.65</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>50</td>
<td>52.20</td>
<td>14.55</td>
<td>33.25</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>75</td>
<td>54.65</td>
<td>9.50</td>
<td>35.85</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>100</td>
<td>56.95</td>
<td>6.30</td>
<td>36.75</td>
<td></td>
</tr>
</tbody>
</table>
to that of 750ml/min, the yield of bio-oil from the pyrolysis with feed of pure corn cobs dropped by more than 20% and that from the pyrolysis with feed of pure HDPE slightly increased. Mulgaonkar [4] found that the sufficient residence time of plastic pyrolysis is between 2-8 seconds. It means that the residence time of the vapour phase was too short for pyrolysis in vapour phase originating from biomass, but sufficient for that from plastics. In terms of maximum temperature, Gao [8] suggests that for polyethylene, polypropylene and polystyrene, the maximum temperature of 450°C, which is less than the prescribed maximum temperature of 500°C in the present work, is enough to produce liquid yield from the pyrolysis. In line with that, Sarker and Rashid [31] have used maximum temperature of 430°C to convert mixture of polypropylene and polystyrene to obtain light grade fractional fuel. However, another parameter was not taken into account in the present work, i.e. temperature non-uniformity of melting plastics in the boat due to low thermal conductivity of plastics. This nature makes heat transfer rate from hot N₂ gas to melting plastic low. The temperature measured in N₂ gas may have been much larger than that measured on the surface of the melting plastics. Many experiments in co-pyrolysis have been done using Thermal Gravimetry Analyser (TGA) [34] in which particle feedstock has high surface area per volume and therefore temperature throughout the feedstock volume can be maintained uniform. Goosey [32] and Ziskind et al. [33] suggested that high melting plastic temperature eases the formation of vapour phase from the melting phase due to low intermolecular forces attributed to long plastic chains. Ziskind et al. [33] also suggested that the rough surface of the melting plastics contributes to diminishing intermolecular forces of the long chain plastic molecules. These suggestions advocate stirring of the mixture of melting plastics and biomass to counteract the conductive heat transfer resistance due to low thermal conductivity of the melting plastics and to oppose high intermolecular forces between plastic molecules.

In the present work, the feedstock was put inside a metal half-cylindrical boat so that the melting plastic material had low surface area per volume of the particles. For this case, the cracking of the particles has to oppose van der Waals forces exerting as intermolecular forces between carbon chains of polymers [35]. In order to overcome this problem, some workers have used high temperature 700°C – 900°C in achieving decent liquid yield [30,37]. In commercial scale, rotary kilns and fluidised beds may have been used for pyrolysis involving plastics in which the surface area per volume of the particles is high [39].

Gas and solid yields obtained from blend of corn cobs and HDPE presented by Table 2 shows that their pyrolysis produced higher yield of solid phase, but lower yield of vapour phase (sum of liquid and gas phases) by increasing plastic composition in feed blend. Most carbons in HDPE are on long straight carbon chains. This structure is more stable than carbon chains with many branches [39,40,41]. The presence of side groups reduces cracking temperature to 450°C for polyethylene [9]. Due to low thermal conductivity of plastics, higher proportion of plastics in the feed blend may have caused larger temperature difference between N₂ gas and the surface of melting plastics. This condition expectedly lowered the release of the vapour phase from the surface of the melting plastics as shown in Table 2. Higher yield of non-condensable gas at higher plastic content in the feed blend is expected to be contributed by biomass pyrolysis because it can start at lower temperature compared to plastic pyrolysis [2,42]. Therefore, even though the feed blend contained more plastics, the plastic material was unable to contribute to the vapour phase yield.

![Fig. 1](image_url)

**Fig. 1** Yield of bio-oil from pyrolysis using blend of HDPE and corn cobs and yield obtained if oils from pyrolysis using pure feeds had been mixed
oils originating from pyrolysis of pure plastics and biomass. In another word, the curve of yields of bio-oil obtained from co-pyrolysis in Fig. 1 in between yields of pure feedstocks is supposed to be higher than the yields calculated by mixing of yields obtained from pyrolysis of pure or separate feeds. If this had occurred, then there would have been synergetic effect between pyrolysis of biomass and that of plastics to improve the bio-oil yield 43 44 and bio-oil quality (bio-oil with less oxygenate content) 45. When the synergy occurs, there are intramolecular and intermolecular hydrogen transfers initiated by free radicals of the plastic pyrolysis followed by mid-chain beta-scissions to decompose biomass and plastic materials 46, Rutkowski and Kubachi 43 concluded that in addition to cracking, there are reactions between radicals formed by both materials which increase the bio-oil yield. In their series of experiments, Zhang et al. 46 47 suspected that the improvement of the bio-oil quality may have been caused by the reactions between olefins formed from the pyrolysis of polyolefin plastics with the radicals from the pyrolysis of biomass in acid-catalysed conditions. The acid conditions formed by the hydrogen donor of the plastic radicals. Therefore, Fig. 1 shows that in the present work, synergetic effect to improve bio-oil yield did not occur.

High peak temperature of 500 °C used in the present work, which is above the peak temperature where mass of the plastics is negligibly decreased according to TGA measurement, i.e. 470 °C for HDPE, supposedly allowed synergetic effect, but it was unattainable. At peak temperature almost all hemicellulose and cellulose were supposedly exhaustedly cracked 48. This problem seems to arise due to low surface area per volume of the plastic particles as explained in Section 3.1. At high temperature, free radicals are more mobile and cleavage of C-C bonds intensifies, which subsequently produce more free radicals 49. Hydrogen atoms supplied by the pyrolysis of plastic material seemed not sufficient to terminate some free radicals to produce more liquid 50.

3.2 Effect of plastic composition in feed blend on compound composition in bio-oil

Table 3 shows the results of the GC-MS analysis on 6 bio-oil products observed on combined non-oxygenate components and combined oxygenate components. The table demonstrates that the higher the composition of plastic feedstock, the higher was the composition of non-oxygenate component in bio-oil. Therefore, the plastic feed contributes to the contents of non-oxygenates. Functional groups identified in bio-oil consist of cycloalkanes, paraffins and olefins as non-oxygenates, and phenols, alcohols, aldehydes, ketones, carboxylate acids, amines and other components as oxygenates as shown in Fig. 2 for feed blend of biomass and HDPE.

Table 3 also shows that at low composition of plastics in feed blend, the yields of oxygenates produced by pyrolysis of blend of HDPE and corn cobs were higher than those obtained if the oils from pyrolysis of pure feedstocks had been mixed. Theoretical non-oxygenates %weight was determined by calculating the composition of the non-oxygenate composition in proportion to the non-oxygenate compositions resulting from the pyrolysis using pure biomass feed A1 and that using pure plastic feed A5. On the contrary, at high composition of plastics in the feed blend, the yields of oxygenates produced by pyrolysis of the feed blend were lower than those obtained if the oils from pyrolysis of pure feedstocks had been mixed. It means that synergetic effect on oxygenates yields occurred in pyrolysis using low plastic content in the feed blend and therefore the plastic radicals in the vapour phase took the role in the synergetic effect when the feed blend contained less plastics.

Bio-oil from feed blend A1 in Table 3 does not contain non-oxygenates because the feed blend was entirely biomass. Bio-oil from feed blend A5 containing only 67% non-oxygenates indicates that HDPE plastic waste contained non-HDPE material containing oxygen atoms. More non-oxygenate products in bio-oil in the pyrolysis using more plastics in the feed blend indicate that in this pyrolysis, more plastic material was cracked to form bio-oil. However, this pyrolysis underwent a condition that conductive heat transfer in the melting plastics was more difficult with larger portion of the plastics in the melting plastics, so that the melting plastic temperature was lower and pyrolysis of the plastic material was more difficult. In turn, it affected the production of hydrogen radicals. As consequences, there was insufficiency of hydrogen supply from plastic radicals to biomass radicals and the formation of oxygenate products was prone to occur. As a result, synergetic effect did not occur in the pyrolysis using more plastics in the feed blend due to less conductive heat transfer.

From different compositions of feed blends, Fig. 2 classifies compounds into 8 different functional groups and miscellaneous oxygenate compounds. Aldehydes, ketones,
alcohols and carboxylates resulted from the cracking of hemicellulose and cellulose, while phenols from lignin constituents.

In general, the trends of compositions of functional groups in bio-oil may be classified into 3 groups, i.e. those with increasing trend at higher plastic composition in the feed blend, those with reducing trend, and those with increasing trend, then reducing at higher composition. The first group consists of cycloalkanes, paraffins and olefins, the second group phenols, alcohols, ketones, and carboxylates, and the third group aldehydes and other oxygenates. Trends attributed to the first and second groups are as consequences of increasing presence of radicals originating from plastic feed and reducing presence of radicals from biomass feed, respectively. Small molecule aldehydes as products of biomass decomposition actually were reactive to the deoxygenation by radicals of plastic pyrolysis. Examination on the compounds of aldehydes by GCMS shows that they consist of furfurals, benzaldehydes and hexadecenal. Furfurals were obtained from the pyrolysis of cellulose and hemicellulose, while benzaldehydes from pyrolysis of lignin. Hexadecenals were obtained from the pyrolysis of plastics. Furfurals and benzaldehydes require high temperature (more than 900°C) to decompose into small molecule compounds and they participate in condensation reaction to form char. It is suspected that high concentrations of furfurals and benzaldehydes in the bio-oil may have occurred as a result of insufficiency of residence time to drive the synergetic effect because these compounds are formed at initial stage of the cellulose and hemicellulose pyrolysis. Similarly, hexadecenals, which contain 16 carbon atoms in their molecules, may also have been in sufficient residence time to decompose. On the other hands, co-pyrolysis with better synergetic effect results in combined composition of furfurals less than that of aldehydes.

3.3 Viscosity and pH of bio-oil

Viscosity and pH tests have been conducted to be compared to those applied in commercial fuels. The viscosity affects flowability of bio-oil and ignition delay time if it would be used as diesel oil. To be used as bio-fuel, bio-oil must not have too low pH, which may cause corrosion on automotive machine components. Bio-oil samples used to viscosity and pH tests were bio-oil from the pyrolysis of feed blends A1, A3 and A5. The results are shown in Table 4.

The table shows that bio-oil from feed blend composing 50% biomass still have pH and viscosity similar to those in diesel oil. Especially for viscosity, gasoline has much lower viscosity than those of diesel oil and bio-oil. The table also shows that the higher the composition of biomass in the feed blend, the higher is the viscosity, but the lower is the pH. It seems that more biomass composition in the feed blend above 50% gives higher rate of increase of the bio-oil viscosity and higher rate of decrease in the pH bio-oil.

The presence of cycloalkanes, alkanes and olefins...
in oil produced by the pyrolysis of plastic feedstock containing C atoms less than 23 in their molecules such as cyclotetradecanes, cyclodecanes, hexacosane, docosanes, and tricosanes contributes to form low viscosity oil and pH nearly 7. On the other hands, oxygenates from biomass feedstock from different functional groups of phenols, furans, alcohols, aldehydes, ketones, carboxylate acids, and amines make bio-oil more viscous. These oxygenates make bio-oil unstable during storage \(^{(6)}\). Polymerization of unstable compounds produces longer carbon chains to produce higher bio-oil. By adding plastics in the feed blend, pH of bio-oil became higher.

4. Conclusions

Some conclusions obtained from the work of co-pyrolysis of corn cobs and HDPE plastics in a fixed bed reactor are as follows:

a. The higher the composition of plastics in the feed blend, the lower is the bio-oil yield.

b. The higher the composition of plastics in the feed blend, the higher is the composition of non-oxygenate mixture of paraffins, olefins and cycloalkanes in the bio-oil.

c. By increasing the composition of plastics in the feed blend, viscosity and pH of bio-oil change approaching to those of commercial diesel oil.

d. Analysis of the synergetic effect indicates that this effect was unattainable both in bio-oil and non-oxygenate yields due to improper conductive heat transfer from N\(_2\) gas to melting plastics.

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