Phase separation of bio-oil produced by co-pyrolysis of corn cobs and polypropylene

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Abstract. In co-pyrolysis of biomass-plastics, bio-oil produced contains both oxygenated and non-oxygenated compounds. High oxygen composition is responsible for instability and low heating value of bio-oil and high acid content for corrosiveness. Aims of the present work are to evaluate possibilities of achieving phase separation between oxygenated and non-oxygenated compounds in bio-oil using a proposed stirred tank reactor and to achieve synergistic effects on bio-oil yield and non-oxygenated compound layer yield. Separation of bio-oil into two layers, i.e. that containing oxygenated compounds (polar phase) and non-oxygenated compounds (non-polar phase) is important to obtain pure non-polar phase ready for the next processing of hydrogenation and used directly as bio-fuel. There has been no research work on co-pyrolysis of biomass-plastic considering possibility of phase separation of bio-oil. The present work is proposing a stirred tank reactor for co-pyrolysis with nitrogen injection, which is capable of tailoring co-pyrolysis conditions leading to low viscosity and viscosity asymmetry, which induce phase separation between polar phase and non-polar phase. The proposed reactor is capable of generating synergistic effect on bio-oil and non-polar yields as the composition of PP in feed is more than 25% weight in which non-polar layers contain only alkanes, alkenes, cycloalkanes and cycloalkenes.

1. Introduction

Co-pyrolysis of corn-cobs and polypropylene plastic is intended to obtain more bio-oil yield and more non-oxygenated compound contents in bio-oil by free radicals interaction of both charges and by hydrogen transfer in which plastic charge is hydrogen donor which transfers hydrogen to biomass charge as hydrogen acceptor [1]. Oxygenated compounds in bio-oil is undesirable for its application as a fuel because they lead to storage instability and low heating value for direct combustion. High carboxylic acids exert high corrosiveness [2]. The present work aims to assess possibilities of attaining phase separation of bio-oil into layers oxygenated compounds (polar phase) and non-oxygenated compound (non-polar phase) as products of a proposed stirred tank reactor and of achieving synergistic effects on yields of bio-oil and non-oxygenated compound layer separated from the bio-oil. This separation is advantageous in obtaining pure non-polar phase for proceeding to hydrogenation or used directly for combustion [3]. There has been no research work on co-pyrolysis of biomass-plastic leading to the phase separation of bio-oil [4]. In co-pyrolysis processing, most of types of reactors used are fixed bed reactors and auger reactors [1]. The selection of reactors for the production of bio-oil should consider the pyrolysis characteristics of feedstock. In the case of feedstock of plastics and biomass, the liquid yield of the plastic and biomass pyrolysis may depend on temperature and heating...
rate of the pyrolysis. According to Lopez et al [5] in their experiment of steam gasification of waste plastics, in which pyrolysis of the plastics was part of gasification, the liquid yield reduced as the temperature of gasification was increased. They worked at 800°C and 900°C. In terms of the effect of heating rate. Hoseini and Dastanian [6] found that liquid yield of the plastic pyrolysis was improved by pyrolysis at lower heating rate. Their work took heating rates spanning from 6 to 14°C/minute using low density polyethylene (LDPE), polypropylene (PP) and polyethylene terephthalate (PET) with final temperature of 500°C. At the lowest heating rate, the liquid yield of LDPE and PP was approximately 80%, while that of PET was 40%. The result of Hoseini and Dastarian’ work suggests that the pyrolysis be carried out at quite low heating rate [6]. For the biomass pyrolysis, in general, Bridgewater [7] noted that higher heating rate of biomass pyrolysis would result in higher yield of liquid product.

Co-pyrolysis of biomass-plastics may produce non-oxygenated compounds in large proportions [8]. Therefore, it is worth investigating how to separate non-oxygenated (non-polar) compounds from oxygenated (polar) compounds in the least cost before the non-polar compounds are further processed to produce bio-fuel. Some researchers in co-pyrolysis suggested that polar and non-polar compounds are difficult to be separated as a result of interactions of radicals derived from co-pyrolysis reactions of their raw materials [4,9]. This difficulty raises efforts to upgrade bio-oil by extracting low molecular weight (MW) oxygenated compounds from bio-oil by adding ethyl acetate [10] or diethyl ether [11] or by water [12]. This separation leaves some large MW oxygenated compounds and hydrocarbons in the bio-oil thus improving stability and heating value of the bio-oil. However, the undertaking could not obtain the quality approaching that of fossil fuels because the bio-oil still contains oxygenated compounds of high MW. Therefore, the bio-oil obtained is restricted to specific uses. An alternative methodology of producing bio-oil by co-pyrolysis is needed so that bio-oil will have quality similar to that of fossil fuels, which contain only hydrocarbons, and will be flexibly produced in terms of its average and range of MW. The undertaking uses phase separation may be an option.

2. Phase separation
In the realm of fluid dynamics, phase separation has been investigated in relation to viscosity and viscosity asymmetry of components of liquids. Lamorgese and Mauri [13] in their simulation work on macroscopically quiescent liquid mixture found that phase separation is easier as the mixture has low average viscosity when the mixture is quenched below a critical point to minimise its mixing free energy. In the co-pyrolysis context, it is suggested that bio-oil have low MW. In terms of viscosity asymmetry, Lamorgese and Mauri [14] found that for the quenching mixture which has a tendency to minimise mixing free energy, at fixed fluidity coefficient of the dispersed phase, increasing viscosity ratio of the dispersed phase to the continuous phase from the unity ratio leads to faster phase separation. On the other hand, at fixed fluidity coefficient of the continuous phase, increasing viscosity ratio leads to slower phase separation. The fluidity coefficient is defined as the ratio of capillary to viscous forces, where the capillary force combines convection and diffusion. This coefficient is proportional to Marangoni number (Reynolds number times Prandtl number) [15]. These two extreme conditions, i.e. the fixed fluidity of the dispersed phase and that of the continuous phase do not occur when vapour phase of co-pyrolysis product is immediately quenched in the condensers. In real co-pyrolysis work, in-between condition occurs because both the oxygenated and non-oxygenated compounds simultaneously make convection by flowing down from the inlet of the condensers as the vapour to the outlet of the condenser as the liquid to enter a bio-oil container. The non-oxygenated compound phase was the dispersed phase, while the oxygenated compound phase was continuous phase in the current work. Whatever conditions, the viscosity asymmetry may induce phase separation. In order to attain phase separation between polar compounds and non-polar compounds, a reactor design with better heat transfer is mandatory which enables to produce bio-oil with relatively low MW range or that with different viscosities between oxygenated and non-oxygenated compounds.

The reduction of viscosity and the enhancement of viscosity ratio between polar and non-polar compounds in bio-oil may be tailored by adjusting the flow of nitrogen gas to the co-pyrolysis feedstock and stirring the pyrolysis feedstock. Heat flux to the reactor feedstock may be improved by
the presence of nitrogen bubbles in the plastic melt, the shear stress at the wall of reactors, and the shear stress in the plastic melt, the latter two of which can be induced by stirring. Zhang et al [16] by their simulation based on experimental database of turbulence intensities in the cores and near the walls of vertical ducts from various researchers concluded that the introduction of gas bubbles to large ducts can induce high local turbulence in the cores, and to small ducts lower local turbulence intensities in the cores, but low local turbulence near the wall. In the case of turbulence on the vertical duct wall, simulations by Tryggvason and Lu [17] and by Mattson and Mahesh [18] found that as the bubbles went up the duct, initially bubbles approached the wall, but then went away from the wall. This indicates that turbulence near the wall occurs at upstream position only.

Simulation by Abbassie [19] suggested that when bubbles rise in low viscosity liquid, the bubble shape and hydrodynamics are dominated by inertial and surface tension forces and the influence by viscous force is neglected. In this case, bubbles are not in spherical shapes and they generate turbulence in the liquid resulting in wobbling/zig-zag motions in the liquid. However, in the viscous liquid environment, the bubble shape and motion are dominated by viscous force in which bubbles retain their spherical shape and no turbulence is generated around the bubbles. By increasing the velocity of bubbles in the plastic melt and reducing the melt viscosity, the average size of the bubbles will increase [20]. Both high velocity and large average size bubbles are favourable to generate turbulence in the plastic melt, which corresponds to the increasing drag and lift forces [21].

In terms of the effect of bubbles on heat transfer, according to Tokunaga et al [22], heat transfer coefficient by the bubbles is much lower (two order of magnitudes lower) than that by liquid. Therefore, high void fraction of nitrogen bubbles in the plastic melt is undesirable. Experiment database acquired by Zhang et al [16] from various researchers suggested that bubble void fraction of max 15% is sufficient to exert high turbulence intensities in the liquid for large diameter ducts. However, the nitrogen bubbles are not expected to reduce plastic melt viscosity, because it requires gas weight fraction of 0.005 or approximately 5 times volume of plastic melt to allow the melt viscosity drop of 20%. Therefore, heat transfer in the plastic melt can rely on improved turbulence intensity in the presence of nitrogen bubbles, but not on reduced bulk viscosity. With sufficient turbulence, it is expected that Biot number, which measures the ratio of the convective heat transfer in the plastic melt to the conductive heat transfer in the biomass particles, becomes high to allow the biomass particle temperature to be approached by plastic melt temperature [23].

Heat transfer enhancement in a co-pyrolysis reactor may adopt that in plastic extruders because they involve in plastic heating. At early process of co-pyrolysis, there is melting conduction, which is a slow process because of very low thermal conductivity of plastics [24]. To accelerate this process, small plastic pellets and good mixing have been suggested [24]. Good mixing can be obtained by rotating the screw of the extruder an optimum rpm (rotation per minute). Rubbing plastic pellets on a heating surface of the extruder as a result of screw rotation induces pellet melting. Large heat conduction near the hot surface and heat convection in the plastic bulk can be enhanced by generating velocity gradient across the radius of the extruder as a result of extruder screw rotation [23].

3. Heat transfer in co-pyrolysis

Two types of reactors generally considered in co-pyrolysis are fixed beds and auger reactors. Fixed bed reactors are mostly designed in the form of tubular reactor [10,4,25] to produce bio-oil in semi-batch mode. No papers have analysed the heat transfer aspect of the fixed bed reactors. Data of different fixed bed reactors suggest that the largest diameter of the reactor ever made is 40 mm and the highest ratio of the height to the diameter is 46. Such a low reactor diameter was designed to overcome low thermal conductivity of the plastic melt in which the heat transfer is governed by heat conduction from the reactor wall to the pyrolysis material. The values of thermal conductivity of PP are between 0.125-0.210 W/(m.K) depending on molecular weight of PP, the higher the molecular weight of PP plastic, the lower is the thermal conductivity of the plastic [26]. Those values of PE are between 0.25-0.33 W/(m.K) [26]. All these values are less than that of water, i.e. about 0.591 W/(m.K). Nitrogen gas in the fixed bed reactor is merely used as sweep gas to bring the pyrolysis vapour out of
the reactors and not considered to improve the heat transfer. The reactor may have had a large temperature gradient in radial direction, if the diameter of the tubular fixed bed reactor had been larger. This heat conduction constraint impedes efforts of scaling up the reactor into commercial scale. It seems that such a heat transfer mode tends to produce bio-oil with some high MW compounds or that with high content of aromatics [10,4,25]. The presence of high MW compounds implies that the heat transfer in the reactors was unable to attain high extent of pyrolysis. The presence of aromatics indicates the combination of plastic free radicals did not sufficiently occur as a result of poor mixing [27]. If the design was maintained for commercial purposes, it required multiple tubular reactors, which are not desirable in terms of investment and maintenance.

Auger reactors are designed to produce bio-oil from co-pyrolysis continuously. To facilitate the continuity of the pyrolysis, at the front end of the reactor there is a hopper to feed the feedstock of the pyrolysis [28]. Inside the reactor, there is a screw to move the feedstock to the rear end of the reactor while it is being heated during its movement to produce different phases of products, i.e. condensable gas, non-condensable gas, char and wax. In most designs, heat is transferred radially from the wall of the reactors into the materials of pyrolysis. Gas nitrogen as a sweep gas flows through the rear end of the reactor to bring out gases through a series of condensers where the condensable gas is converted into bio-oil. The designs of reactors suggests that the heat transfer to the plastic melt is governed by laminar heat convection in radial direction while plastic melt and biomass particles loaded in the plastic melt flow in axial direction. It seems that heat flux in the auger reactors is not sufficiently high to heat up pyrolysis materials. The bio-oil obtained by previous researchers still contained mixed oxygenated and non-oxygenated compounds with some high MW compounds or that with high content of aromatics [4,28,29].

A reactor design alternative to the fixed bed and auger reactors is worth proposing to overcome the heat transfer constraints in these types of reactors. Considering elucidation of heat transfer above, a stirred tank reactor equipped with nitrogen flow to induce local turbulence may be a better option for co-pyrolysis of biomass and plastics. In this case, the heat transfer is dominated by turbulent heat convection, which is different from the previous reactors, which used heat conduction and laminar heat conduction. Temperature and heating rate of the feedstock, which is contributed by the heat flux, determines the extent of the reactor feedstock cracking [30].

4. Experimental
Corn cobs obtained from an agricultural waste were ground and sieved to a particle size of 8 – 50 mesh. The particles were then dried in an oven so that the moisture content reached ≤ 10%. Meanwhile, the PP granules used in the experiment were of 3 mm average diameter. Unlike the corn cobs, the PP granules were not pre-treatment prior to pyrolysis.

Table 1. Proximate and ultimate analysis of the feedstock (air-dried basis).

| Analysis Parameter         | Corn Cobs (%weight) | Polypropylene (%weight) |
|----------------------------|---------------------|-------------------------|
| Proximate analysis         |                     |                         |
| Air-dried moisture         | 11.02               | 0.11                    |
| Ash                        | 5.07                | 0.00                    |
| Volatile matter            | 69.31               | 99.89                   |
| Fixed carbon               | 14.60               | 0.00                    |
| Ultimate analysis          |                     |                         |
| C                          | 41.07               | 87.18                   |
| H                          | 6.54                | 12.70                   |
| N                          | 0.76                | 0.03                    |
| Total sulphur              | 0.09                | 0.07                    |
| O*                         | 46.47               | 0.02                    |
| H/(C+H+O+N) atomic ratio   | 0.07                | 0.13                    |
Ultimate analysis and proximate analysis of feedstock are given in table 1. Data of proximate analysis show that corn cobs are composed of mainly volatile matter, which allows high yield of bio-oil [31]. Data of ultimate analysis show that atomic ratio of H in corn cobs is nearly a half of that in PP. In co-pyrolysis of corn cob particles and PP granules, the corn cob particles are deficient in hydrogen, whereas PP granules contain more hydrogen as seen in their atomic ratios of hydrogen. The hydrogen excess provided by PP exerts two effects against bio-oil produced by biomass alone, the first, it improves hydrogen atmosphere in pyrolysis reactions resulting more bio-oil yield [32] and the second, it partly removes oxygen radicals derived from biomass pyrolysis thus improving non-oxygenated compound composition in bio-oil [33].

To perform co-pyrolysis in the stirred tank, feedstock charges of corn cob particles and PP granules were varied at 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%, and 100% weight of PP. A schematic of the co-pyrolysis experimental rig is shown in figure 1. In all runs of co-pyrolysis, 250 grams of feedstock were charged to the stirred tank reactor at heating rate of 5°C/minute from ambient temperature to 500°C, with a holding time of 10 minutes after the peak temperature to allow further pyrolysis of the remaining feedstock in the reactor. The flow of nitrogen gas was maintained at 500 ml/minute, which had been proven obtaining maximum oil yield using plastic feedstock. A faster flow of nitrogen is likely to lead to a shorter residence time in the vapor phase for interaction between free radicals of biomass and plastic to attain a synergetic effect. Conversely, if the flow rate of nitrogen is too low, it could trigger a secondary pyrolysis reaction in the reactor due to an excessively long residence time leading to production more char [7,34]. The rotation rate of the two-paddle stirrer was 100 rpm. The resulting pyrolysis vapor was condensed in a series of two water-cooled bulb condensers and the bio-oil produced was collected in a vacuum flask. Cooling water at 15°C was used in the condensers. At the end of each experiment run, the liquid product was weighed, separated into 2 samples for that bearing phase separation and analysed using GCMS analyser.

Figure 1. Experimental rig of co-pyrolysis.

5. Results and discussion

5.1. Synergistic effect on bio-oil yield
Experiment of co-pyrolysis corn cob particles and PP plastic have resulted bio-oil samples with low yields from co-pyrolysis using feed containing 0 and 12.5% PP and yields increasing at increased PP composition in the feedstock from 12.5% to 87.5%. The bio-oil yield slightly reduces as the pyrolysis uses pure PP. The effect of PP composition on the bio-oil yield is described by figure 2. Comparing the bio-oil yields obtained experimentally from co-pyrolysis and those calculated based on
experimental yields using pure feedstock and proportional to the compositions of PP in the feeds will give insight about synergistic effect of the co-pyrolysis on the bio-oil yield. Figure 3 shows that the synergistic effect is favoured as the PP composition is more than 25%. Setting heating rate as low as 5°C/min also assists to retain plastic melt in the reactor in close contact with biomass particle which is favourable to attain high oil yield [35]. Therefore, in co-pyrolysis involving high portion of PP in the feedstock, the yield of bio-oil increases and that of char reduces as the PP composition in feed increases. The regime where co-pyrolysis using feeds containing PP 25% and less is subsequently called as regime I, and that using feeds containing PP 37.5% and more as regime II.

![Figure 2. Yields of co-pyrolysis products as function of PP compositions in feeds.](image)

![Figure 3. Synergistic effect of co-pyrolysis on bio-oil yield.](image)

5.2. Synergistic effect on non-oxygenated phase yield
In terms of hydrogen balance, plastics as hydrogen donor transfer hydrogen atoms to biomass to produce bio-oil with more non-oxygenated compounds [33]. Squir et al [36] and Matzakov [37] found that as the free radicals of a hydrogen acceptor exceed the capacity of the hydrogen acceptor to catch
hydrogen atoms, then the free radicals combine or attack available large molecules to bear cross-linking reactions which produce secondary char. Figure 4 shows the result of the hydrogen transfer as well as the phase separation of the bio-oil in the present work where the upper layer of the bio-oil container composes non-oxygenated compounds, while the lower layer oxygenated compounds. Comparison of PP compositions in the feeds and corresponding non-polar % volume also in regime II exhibits the existence of synergistic effect on the non-polar bio-oil where % volume of non-polar layer is always higher than %PP in the feedstock.

**Figure 4.** Synergistic effect of co-pyrolysis on non-oxygenated compound phase.

Measurement of viscosity of polar layers from co-pyrolysis in the present work using various feed compositions demonstrated that they have very similar viscosities with average of 1.1 cStokes and % standard deviation of 2.7%. Those values for non-polar layers are 2.03 cStokes and 6.4%. Comparison of average viscosities of polar and non-polar layers shows that there is viscosity asymmetry between the polar layers and the non-polar layers where the viscosities of the polar layers are smaller than those of the non-polar layers. The magnitudes of these average viscosities are considered low because they are within the range of gasoline viscosity of approximately 0.7 cStokes and diesel oil viscosity of approximately 2.7 cStokes. Both low viscosities of polar and non-polar layers and viscosity asymmetry of these layers in the present work induced the phase separation between polar and non-polar layers [13,14]. This is very advantageous because physical separation between these layers shortly after the formation of bio-oil is no longer needed. In contrast, most of the previous co-pyrolysis works have never reached such phase separation thus requiring complicated bio-oil phase separation because of introduction of new solvent [10-12].

The viscosity difference may be inferred by figures 5 and 6. Figures 5 and 6 show % total area against retention time interval limit extracted from GCMS analysis of the polar layer and the non-polar layers of bio-oil samples, respectively. The value 1 is the upper limit of the retention time interval from 0 to 1 minute, 2 the upper limit of the interval from 1 to 2 minutes, and so on. Comparison between these figures demonstrates that the maximum retention times of the non-polar layers are about twice those of the polar layers. This indicates roughly that the longest carbon chains of compounds in the non-polar layers are longer than those in the polar layers. Figure 5 indicates that qualitatively the polar layers compose mostly shorter carbon-chains of oxygenated compounds described by the left skewness of the curves, whereas figure 6 indicates the total area roughly descends gradually from the highest at the lowest retention time to the highest retention time. The presentation of curves in figures 5 and 6 suggests that the carbon-chain distributions in the polar layers of bio-oil samples taken from
co-pyrolysis of various PP compositions in the feeds are very similar, but fluctuated in the non-polar layers. These levels of similarities are also implied by the values of %standard deviation of various viscosities, which were 2.7% for viscosities of the polar layers and 6.4% for those of the non-polar layers.

**Figure 5.** Total area percentages of oxygenated compounds acquired from GCMS analysis.

**Figure 6.** Total area percentages of non-oxygenated compounds acquired from GCMS analysis.

5.3. Bio-oil composition

Figures 7 and 8 exhibit the compound compositions based on functional groups for oxygenated compounds (in the polar layers of bio-oil samples) and types of carbon chains for non-oxygenated compounds (in the non-polar layers of bio-oil samples). Figure 7 shows that main compounds in the polar layers are carboxylic acids, furans, ketones, guaiacols, and phenols. The compositions of these compounds vary at different compositions of PP in feeds, but in general the rank of compositions from the highest is carboxylic acids, furans and interchangeably between ketones, guaiacols and phenols.
Carboxylic acids are obtained from pyrolysis of cellulose, hemicellulose and lignin, while furans from pyrolysis of cellulose and hemicellulose. Both carboxylic acids and furans are formed at mild condition (approximately 300°C) [38]. Guaiacols and phenols are obtained from pyrolysis of lignin at more severe condition approaching 500°C [38]. Therefore, most of compounds were produced at mild conditions. Approximate analysis data in table 1 show that nearly 70% of biomass contains volatile matters, which are mostly from pyrolysis of cellulose and hemicellulose [39] and most of them seem to be cracked at mild condition. Ketones and aldehydes are mainly produced from pyrolysis of levoglucosan (originated from cellulose as parent structure) [40]. These compounds are readily hydrogenised towards more stable groups [41] leading to their small compositions in the bio-oil. Abella et al [40] found that activation energy towards the formation of aldehydes is high and their presence in the bio-oil therefore depends on how heat flux to biomass particles occurred.

Figure 7. Compositions of oxygenated compounds in bio-oil acquired from GCMS analysis.

Figure 8 exhibits the compositions of non-oxygenated compounds in the non-polar layers of bio-oil. GCMS analysis noted that there are four main types of hydrocarbons in the non-polar layers, i.e. alkanes, alkenes, cycloalkanes and cycloalkenes, which were produced from PP plastic pyrolysis. In case of thermal cracking, the cyclisation leading to the formation of cycloalkanes and cycloalkenes is promoted by free radical mechanism [42]. No aromatics have been produced from plastic degradation in the co-pyrolysis. This indicates that there was no methyl branching leading to aromatisation or methyl groups combine each other to form oligomers as non-condensable gas, which otherwise are contributed by the presence of Pt-containing catalyst at 525°C. [27]. Crosslink of the plastic free radicals may have also not occurred in regime II as described by the diminishing wax yield as the PP composition was increased [43]. For regime II, the compositions of hydrocarbons taken from co-pyrolysis at various PP compositions in the feds are similar or nearly identical. It seems that part of plastic free radicals give away their hydrogen to biomass free radicals to add up non-oxygenated compounds. This phenomenon has been predicted to occur by Bhattacharya et al [28] and Chen et al [44].
Figure 8. Compositions of non-oxygenated compounds in bio-oil acquired from GCMS analysis.

6. Conclusions
The present work of co-pyrolysis of corn cob particles and PP granules in the proposed stirred-tank reactor results in some conclusions as follows:

- The reactor is capable of producing bio-oil with low viscosity and viscosity asymmetry leading to phase separation between oxygenated and non-oxygenated compounds.
- Synergistic effect has been achieved on yields of bio-oil and non-polar layer of the bio-oil for co-pyrolysis using feeds containing more than 25% weight of PP.
- Using settings of stirrer rotation of 100 rpm and flow of nitrogen of 500 mL/min, non-polar layer contains only alkanes, alkenes, cycloalkanes and cycloalkenes. This layer may be used as a biofuel due to the absence of oxygenated compounds.

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