Formation of non-oxygenated phase of bio-oil produced by co-pyrolysis of corn cobs and polypropylene plastic using zeolite catalysts at low heating rate

Dijan Supramono, Aisyah Fadhlillah, Mohammad Nasikin*
Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia
*Corresponding author: mnasikin@che.ui.ac.id

Abstract. Thermal co-pyrolysis of corn cobs and polypropylene (PP) at low heating rate (thermal slow co-pyrolysis) has succeeded in separating bio-oil produced between oxygenated and non-oxygenated phases spontaneously. In co-pyrolysis, PP can sequester oxygen from bio-oil to convert part of bio-oil to non-oxygenated phase and can contribute partly non-oxygenated phase by PP carbon chain cracking. Catalytic fast co-pyrolysis has been commonly used to improve bio-oil yield and to improve non-oxygenated fraction of bio-oil. However, the catalytic fast co-pyrolysis is unable to obtain separate non-oxygenated fraction of bio-oil. In present work, zeolite catalyst was introduced in co-pyrolysis of corn cobs and PP at low heating rate to undertake catalytic slow co-pyrolysis in order to obtain synergistic effect of non-oxygenated fraction of bio-oil while obtaining separate non-oxygenated fraction of bio-oil. The present co-pyrolysis work was carried out in a stirred tank reactor at heating rate of 5 °C/min and maximum temperature of 500 °C. The composition of feed was varied at 0, 50 and 100%PP in the mixture of corn cob particles and PP granules. The experiment involved 3 catalytic configurations, i.e., no catalyst, ZSM5-38 and ZSM5-70, in which 38 and 70 represents the mole ratio of Si/Al in the catalysts. The results show that in slow co-pyrolysis of biomass-PP, the use of zeolite catalyst with high acidity suppressed the pyrolysis of PP to form wax and reduced bio-oil yield, and the synergistic effect was obtained as the co-pyrolysis used no catalyst and zeolite catalyst of ZSM5-70, while that using zeolite catalyst of ZSM5-38reached negative synergistic effect. Utilization of catalyst generated high amount of aliphatic moieties, i.e. methyl, methine and methylene. With ZSM5 catalyst utilization, production of allyl decreased. Most of non-polar bio-oil fractions have similar or slightly higher heating values (HHVs) compared to those of commercial fuels. Branching index (BI) values of non-polar phase of bio-oil generated straight carbon chain with higher branches compared to those commercial fuels.

1. Introduction

As several sectors like transportation, industry and commercial are growing, the dependency on utilization of fossil fuel also increases. Meanwhile in Indonesia, reserved fossil fuel continued to decrease from 5.9 billion barrels in 1995 to 3.7 billion barrels in 2015. With the present production rate and no new reserve fossil fuel discovered, Indonesia will run out of fossil fuel reserve in 11 years. The limitation of fossil energy resources, the transition to new and renewable energy resource is an inevitable option [1].

Biomass is one of potential new and renewable energy sources as substitute to fossil energy. It is estimated in 2050 the world primary energy will be mostly generated from biomass [2]. According to Safana et al [3], biomass is the only source that can be converted into liquid, solid as well as gasfuels. Pyrolysis is one of alternative technologies used to convert biomass into fuel. It produces bio-oil, char
and non-condensable gas, which may be further processed to form fuels. However, bio-oil produced from pyrolysis of biomass contains oxygenated compounds which has low heating value, corrosive and unstable fuel properties [4][5]. To overcome this shortage, the addition of a hydrogen-rich co-reactant such as olefinic plastics can significantly increase the quality of bio-oil by removing oxygen content in bio-oil [6]. PP is one of most abundant olefinic plastic wastes and it contains tertiary carbons which favour hydrogen and methyl donation during thermal degradation [7].

The preceding work on thermal co-pyrolysis at low heating rate (slow co-pyrolysis) shows that there is phase separation between oxygenated and non-oxygenated fractions which cannot be achieved by fast co-pyrolysis, commonly used to improve the yield of bio-oil [8]. The non-oxygenated fraction is precursor of the formation of biofuel because it contains hydrocarbon only. The use of catalyst of micro-pore ZSM5 zeolite in biomass fast pyrolysis has been proved to improve non-oxygenated fraction of bio-oil and result in bio-oil with much less aromatic content [9] and in slow pyrolysis high density polyethylene limit the highest molecular weight of oil to obtain oil similar to gasoline [10]. These effects favour the formation of non-oxygenated bio-oil for biofuel. In the present work, the catalysts were applied to slow co-pyrolysis to investigate its effect on the yield and composition of non-oxygenated fraction of bio-oil. It is hypothesized that such a slow catalytic co-pyrolysis would result in phase separation between oxygenated and non-oxygenated fractions in bio-oil and improve synergistic effect on non-oxygenated fraction, in which fraction of non-oxygenated fraction of bio-oil obtained from co-pyrolysis was higher than that obtained from combined bio-oil yields of biomass and PP. In authors’ knowledge, catalytic co-pyrolysis of biomass-PP at low heating rate has not been investigated to see how it affects synergistic effect on the yield of non-oxygenated fraction of bio-oil and how close the composition of the non-oxygenated fraction to that of commercial fuels. The present work was aimed at investigating effect of catalyst addition in slow co-pyrolysis on the yield of non-oxygenated fraction of bio-oil as well as on the characteristics of non-oxygenated fraction in relation to its utilisation as biofuel.

The surface area, acidity, pore size and volume are the key factors of catalyst affecting pyrolysis process. Lower Si/Al ratio in zeolite catalysts leads to higher total acidity of catalyst. These characteristics favour in polyolefin cracking [11].

2. Materials and Experiment

2.1 Feedstock Materials

Corncob particles used in this research were obtained from agricultural waste and already has been grounded. They were prepared by drying in an oven at 105 °C to reach 10% moisture content. PP oval granules used in this experiment were of virgin PP with granule size of 2.5 x 4 mm. The shape of granules in slow pyrolysis was expected not to affect the co-pyrolysis results because the granules had sufficient time to melt before they were decomposed at about 400 °C [12]. Proximate and ultimate analysis data of the present feedstock materials can be found elsewhere [8]. Data in the proximate analysis shows that corncobs 63.91% of volatile matter, which allowed high production of bio-oil.

Catalysts used in the present research were ZSM5 with two different Si/Al ratios, 38 and 70. The characteristics of the catalysts were identified by Si/Al mole ratio, surface area, pore volume and pore size shown in Table 1. ZSM5 characteristics obtained from catalyst supplier Jiangsu XFNANO Materials Tech Co., Ltd.

| Catalyst | Si/Al | Specific Surface Area (m²/g) | Pore Volume (mL/g) | Pore Size (nm) |
|----------|-------|-------------------------------|--------------------|---------------|
| ZSM5     | 70    | 400                           | 0.35               | 0.58          |
| ZSM5     | 38    | 330                           | 0.15               | 0.53          |
2.2 Experiment

The present co-pyrolysis work was carried out in a stirred tank reactor at heating rate of 5 °C/min, peak temperature of 500 °C and holding time of 10 minutes at the peak temperature. Nitrogen flow was maintained at 750 ml/min throughout the experiment batch. Feed used in the present research was kept 250 grams every batch and composition of feed was varied at 0, 50 and 100% PP in the mixture of corn cob particles and PP granules. Loading of catalyst in feed was 5% in the premix of PP and biomass. For comparison, non-catalytic (thermal) co-pyrolysis was also conducted. The resulting pyrolysis vapour 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 10-15°C was used in the condensers. The arrangement of experimental rig has been addressed elsewhere [8].

3. Result and Discussion

3.1 Yield and Synergetic Effect of Bio-Oil

Figures 1a to c show yields of pyrolysis and co-pyrolysis products involving 3 different feed compositions. Figure 1a shows that using 0%PP feed or pure biomass and 3 different catalysts (no catalyst, ZSM5-38 and ZSM5-70), the yields of bio-oil and non-condensable gas were very similar. In comparison, wax yield decreased and char yield increased with catalyst addition. The use of ZSM5 prepared acid sites on catalyst pore surfaces, in which the higher the mole ratio of Si/Al, the less is the acidity generated [13]. According to Anca-Couce et al [14], slow pyrolysis of biomass generated secondary reactions in series with primary pyrolysis. They found that secondary char formed by radicals from primary pyrolysis can deposit on the biomass char surface resulting in blocking of active sites of the biomass char, which reduces reactivity of the char. Secondary reactions include dehydration, re-polymerisation and re-condensation to form char, non-condensable gas and water [15]. The presence of catalyst in biomass fast pyrolysis could reduce the possibility of re-polymerisation of primary pyrolysis products to form char [16]. However, in the present work, as shown in Figure 2a, the presence of catalyst tended to promote the formation of char which possibly obtained from re-polymerisation of primary pyrolysis products. It seems that high yield of secondary pyrolysis products in long residence time in slow pyrolysis reactor promoted re-polymerisation to form more char.

Figure 1b. shows 50%PP co-pyrolysis yield. It shows bio-oil yield of co-pyrolysis 50%PP with ZSM5-38 addition produced the lowest bio-oil yield compared to other catalyst configuration. The catalyst with low mole ratio of Si/Al was expected to give the highest acidity. The presence of ZSM5-38 catalyst reduced the yield of bio-oil derived from biomass and PP pyrolysis. It seems that high acidity in slow co-pyrolysis was not effective to induce hydrogen transfer from PP pyrolysis to biomass pyrolysis products to improve bio-oil yield. This is in contrary to the result of non-catalytic co-pyrolysis, which resulted in higher yield of bio-oil. The lower contribution of PP on bio-oil in co-pyrolysis using ZSM5-38 was expected with higher formation of wax. In other words, PP pyrolysis was suppressed in high acidity condition in the presence of biomass to form wax.

Yields of co-pyrolysis using 100%PP feed are shown in Figure 1c. Addition of the zeolite catalysts in pyrolysis of 100%PP affected wax production and for this case Figure 1c shows that no wax was generated from pyrolysis using zeolite catalysts. In terms of liquid and non-condensable yields, Figure 1c shows that the addition of the catalysts reduced the earlier and increased the latter. Gaurh and Pramanik [17] found similar results for non-condensable gas and liquid. It seems that acidity of the catalysts enhanced cracking of PP compounds to form smaller compounds. However, the acidity variation due to difference in Si/Al mole ratio did not sensitively affect product distribution of PP pyrolysis in the present reactor. Miandad et al [18] found that high acidity of catalyst reduces the liquid yield, but increases the gas yield. The different reactor configurations may have affected different liquid yields. In the present work, a stirred tank reactor was used with the height to the diameter ratio of 2. It seems that lighter compounds obtained from pyrolysis using higher acidity catalyst re-condensation to form larger compounds.
Figure 1. (a) Yield of pyrolysis 0%PP composition in feed as function of catalyst type (b) Yield of pyrolysis 50%PP composition in feed as function of catalyst type (c) Yield of pyrolysis 100%PP composition in feed as function of catalyst type
Knowing bio-oil yields produced in experiment, synergistic effect can be obtained by comparing percentage of non-polar phase bio-oil with that obtained theoretically if feeds of equal weights of PP and biomass had been pyrolyzed separately. Figure 2 shows the synergistic effect only occurred in co-pyrolysis involving no-catalyst and ZSM5-70. Synergistic effect occurs because of hydrogen transfer from plastic pyrolysate to biomass pyrolysate and it led to hydride-oxygenation part of oxygenated compounds into non-oxygenated compounds. The existence of hydrogen free radical expelled oxygen and allowed to produce more non-oxygenated compounds [19]. Negative synergistic effect in co-pyrolysis using ZSM5-38 catalyst in accordance with the wax yield exhibited by Figure 1b indicates that co-pyrolysis in high acidity adversely suppressed the pyrolysis of PP and therefore PP did not contribute to improve the yield of bio-oil.

3.2 H-NMR Analysis for Non-Polar Fraction

Figure 2 shows H-NMR analysis result of non-polar phase bio-oil indicating compositions of H attributed to chemical bonds or carbon chains in non-polar phase of bio-oil. It can be seen that there are five moieties within the non-polar phase bio-oil, i.e., methane (CH), methyl (CH₃), methylene (CH₂), vinyl (C=C), allyl (α-C to C=C), aromatic and benzylic (α-C to aromatic ring). In all co-pyrolysis batches with varying catalyst types, H attributed to methyl comprised the highest percentage followed by methine.

![Figure 2. Synergistic Effect of non-polar phase of co-pyrolysis PP-corncobs with various catalyst type](image)

![Figure 3. H-NMR analysis result of co-pyrolysis on non-polar bio-oil](image)
Figure 3 shows that non-polar phase of bio-oil mostly contained H attributed to methyl, methylene and methine which are part of alkanes. High yields of H attributed to methyl, methylene and methane indicates that most content of non-polar phase was of primary reaction regime [19]. Addition of catalyst slightly decreased the amount of alkane, which reduced original carbon chains. The presence of H attributed to allylic bonds indicates more alkene carbon chains. Figure 3 shows that utilization of ZSM5 of both ratios of Si/Al of 38 and 70 slightly decreased the production of allyl. It indicates that the utilization of catalyst suppressed the generation of alkenes. The presence of H attributed to benzyl showed rather similar values in all co-pyrolysis with different catalysts. The presence of benzylic H shows that there was aromatic generation within the pyrolysis process originating from lignin pyrolysis [20].

3.3 Properties of Non-Polar Fraction

Table 2 shows properties like HHVs and branching indices of non-polar phase arising from the current work in comparison with those of commercial diesel fuel and gasoline. HHV is an important property of fuel which defines the energy content of fuel [21]. HHV can be calculated with equation below:

\[ HHV = 0.328C + 1.419H + 0.0928S \] (1)

Both of commercial fuels have similar values of HHV of around 47 MJ/kg, as stated in Table 2, most of HHVs of non-polar phase of bio-oil have similar values or slightly higher than that of both commercial fuels. Therefore, no much differences in terms of HHV of all bio-oil types and commercial fuels. Table 2 also provides BI values which identify carbon chain characteristics. The lower BI value indicates the longer carbon chain and heavier molecule weight [22]. From data served in Table 2, 50%PP+ZSM5-38 had similar BI value to commercial gasoline. Most of all non-polar fractions of bio-oil had higher BI values compared to that of commercial fuels which indicates that non-polar fractions of bio-oil may have had shorter straight carbon chain with more branches than those of commercial fuel.

Catalytic co-pyrolysis at high heating rate has been conducted by Xue et al [23] using polyethylene (PE) as hydrogen donor and zeolite catalyst of HZSM5. They found synergistic effect on hydrocarbon yield and suppressed coke formation. Using cellulose as part of biomass and PE, they found that there was increase of aromatic hydrocarbon yield until 20%, but no increase in total aliphatic hydrocarbons. They suspected that reaction of Diels Alder had been predominant in co-pyrolysis. Using lignin as part of biomass and PE, their results show that there was increase in both aromatic and aliphatic hydrocarbons until 40%. However, the phase separation did not occur and this may have been caused by high composition of aromatics in bio-oil.

Until now research in biomass pyrolysis and co-pyrolysis of biomass-polyolefins have not been conducted to investigate the whole energy balance starting from feedstock until pyrolysis products. The research mostly involved how to get non-oxygenated fraction as much as possible by using thermal or catalytic pyrolysis or co-pyrolysis. In small scale, it has been known that pyrolysis of lignin and hemicellulose as part of biomass exhibit exothermic reactions, while cellulose endothermic reactions unless primary products undergo secondary reactions [24]. On the other hands, polyolefin pyrolysis is endothermic reaction [25]. Co-pyrolysis may be better approach both in improving non-oxygenated fraction yield and heat integration.
Table 2. Property of non-polar bio-oil fraction

| Variable                  | HHV (MJ/kg) | BI  |
|---------------------------|-------------|-----|
| 100% PP                   | 47.34       | 0.94|
| 50% PP                    | 47.56       | 1.05|
| 50% PP + ZSM5-70          | 48.09       | 1.18|
| 50% PP + ZSM5-38          | 47.08       | 0.99|
| Commercial diesel fuel    | 47.95       | 0.4 |
| Commercial gasoline       | 47.83       | 0.98|

4. Conclusion

Some conclusions have been obtained from the present work where catalytic slow co-pyrolysis of corn-cobs-PP has been conducted. In terms of product yields of slow pyrolysis of biomass, the addition of zeolite catalysts increased the yield of char. In slow co-pyrolysis of biomass-PP, the use of zeolite catalyst with high acidity suppressed the pyrolysis of PP to form wax and reduced bio-oil yield. In slow pyrolysis of PP, the use of zeolite catalyst reduced liquid yield and increased non-condensable gas yield significantly.

Synergistic effect on the yield of non-oxygenated fraction of bio-oil was obtained as the co-pyrolysis used no catalyst and zeolite catalyst of ZSM5-70, while that using zeolite catalyst of ZSM5-38 reached negative synergistic effect. Utilization of catalyst generated high amount of aliphatic moieties in non-oxygenated fraction, i.e. methyl, methine and methylene. With ZSM5 catalyst utilization, production of allyl decreased. Most of non-oxygenated bio-oil fractions have similar or slightly higher heating values (HHVs) compared to those of commercial fuels. Branching index (BI) values of non-polar phase of bio-oil generated straight carbon chain with higher branches compared to those commercial fuels.

Acknowledgement

The author would like to express their gratitude to Universitas Indonesia for its financial support to the current work through PITTA (Publikasi Terindeks Internasional untuk Tugas Akhir Mahasiswa) scheme with contract no. NKB-0065/UN2.R3.1/HKP.05.00/2019 for the budget year 2019.

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