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Previously, there has been no research conducted on the compositions of non-polar and polar fractions of bio-oil produced by co-pyrolysis of biomass and plastic as the feeds in relation to the variation of N_2 gas carrier flow rate. Corn cobs was used to represent biomass and polypropylene (PP) plastic was used as hydrogen donor in the co-pyrolysis. Co-pyrolysis was conducted in a stirred tank reactor at heating rate of 5ºC/min. Bio-oil separated into non-oxygenated (non-polar) fraction and oxygenated (polar) fraction. Non-polar fraction can be further processed as bio-fuel, while the polar fraction can be refined to produce different chemicals. The aim of the present research is to investigate the effect of N_2 gas flow and feed composition on the composition of polar and non-polar phases of bio-oil. More gas flow rate reduced the vapor phase residence time in the co-pyrolysis reactor. N_2 gas flow rate was varied 400, 500 and 600 mL/min with each flow rate performed in 3 different ratios of biomass-plastic feed compositions, i.e. 0%: 100%, 50%: 50%, and 100%: 0%. The higher N_2 gas flow rate resulted in higher bio-oil yield but lower char yield. Co-pyrolysis favored synergistic effect on non-polar phase yield and lower N_2 gas flow resulted in more synergistic effect. The maximum non-polar fraction addition from its theoretical fraction in bio-oil was 35%. For non-polar phase of bio-oil, GC-MS analysis shows that alkenes were predominant in light fraction of bio-oil, while H-NMR shows that methyl chain was predominant in bio-oil. For polar phase of bio-oil, GC-MS analysis shows that carboxylic acids were predominant in light fraction of bio-oil, while H-NMR shows that carbohydrates were predominant in bio-oil. To utilize non-polar phase of bio-oil as biodiesel, branching index needs to be reduced about one third to a half and double bonds of alkene content needs to be decreased from the present content of 6-7% mole. Co-pyrolysis allows the reduction of phenolic content in polar phase of bio-oil arising more dominance of carbohydrate in the polar phase of bio-oil.

Keywords: Biomass, Bio-oil, Polypropylene Plastic, Slow Co-Pyrolysis

1. Introduction

The process of biomass pyrolysis has been widely studied, but biomass pyrolysis has disadvantages because it produces bio-oil which has high oxygen, acid and high water content[1)]. Therefore, we need to improve the quality of bio-oil by combining the pyrolysis of biomass with organic compound which has high hydrogen content. Plastics are one of the ingredients that contain more hydrogen and lower water content in the pyrolysis[2)]. Moreover, the knowledge of inclusion of plastics in co-pyrolysis can be considered as an attempt of lessening ignorance as a fundamental cause of environmental destruction as the effect of widespread use of plastics[3)]. The presence of plastic in co-pyrolysis will reduce the oxygen content and makes bio-oil have characteristics similar to fossil fuels. In the research of Supramono et al[4)] the slow co-pyrolysis process of corncob and PP plastic produces bio-oil which can separate into 2 phases, polar phase and nonpolar phase. The latter can be improved to biofuel, while the former has not been widely used because it contains versatile functional groups with various compositions. In terms of viscosity, bio-oil synthesized by slow pyrolysis is much lower than that by fast pyrolysis. Supramono et al[4)] have succeeded to separate non-polar fraction from polar fraction and found that viscosity of non-polar phase of bio-oil obtained from slow pyrolysis measured at 40ºC could reach 1.1 cStokes, while that of non-polar phase 2.03 cStokes. The phase separation enables to acquire non-oxygenated compounds which can be further processed to produce bio-fuel. In comparison, viscosity of bio-oil obtained from fast pyrolysis can vary from 25 to 1000 cSt[5)]. This condition of high average viscosity makes spontaneous separation between oxygenated and non-oxygenated fractions of bio-oil become difficult[6)]. Ben and Ragauskas (2013) found that at high temperatures (400-600ºC), slow pyrolysis of pine wood and kraft lignin produce bio-oil containing molecules with average molecular weights about a half of those of molecules in bio-oil obtained from fast pyrolysis[7)]. Lower molecular weight affects proportionally to the reduction of viscosity. Therefore, slow pyrolysis is beneficial to produce non-polar fraction with low viscosity much easier. The present study was investigating how co-pyrolysis between biomass represented by corn cobs and plastic material represented by polypropylene (PP) affects functional group composition in polar phase and carbon chain type composition in non-polar phase. Composition observation was done upon light oil as part of the bio-oil as well as upon the whole bio-oil. The earlier oil can be analyzed by GC-MS, while the latter oil by H-NMR. High molecular weight compounds, some of which are carbohydrates and lignin-derived oligomer, are not amenable to GC-MS analysis due to their high boiling point[8)]. This intrinsic characteristic of GC-MS allows analysis of light oil as part of bio-oil.

Bio-oil composition may be affected by different carrier gas flow rates in pyrolysis. Slow pyrolysis instigates low severity of pyrolysis of biomass and consequently low pyrolysis kinetics. Such a low kinetics requires long residence time to allow secondary pyrolysis to occur in the reactor. In the study of fast pyrolysis of biomass by Kan et al[9)]. The pyrolysis with a large N_2 flow rate causes a short vapor phase residence time and secondary pyrolysis products may not be complete from hemicellulose and cellulose to a temperature of 500ºC. However, at lower N_2 flow rate, the pyrolysis occurs in longer vapor phase residence and the pyrolysis reaction continues to secondary pyrolysis. There have been no previous studies examining the effect of carrier gas flow rate on the composition of bio-oil in slow process. The present study is aimed of investigating effect of feed composition and flow rate of N_2 carrier gas on the composition of bio-oil both in polar and non-polar phases. The feed composition was varied 0%, 50% and 100% PP in the feed blend of corn cobs and PP. This study also analyses the possibility of acquiring non-polar phase with low alkene composition and attaining predominance of functional groups in polar phase. The earlier was concomitant with possibility of utilizing non-polar phase for biofuel, while the latter possibility of the ease of functional group separation.

2. Experimental

The slow co-pyrolysis process in this study used corncob and PP plastic. Corncob underwent a pre-treatment process until the particle size is 8-50 mesh. Then, the particles were dried in an oven so that the water content reaches ≤ 10%. Meanwhile, PP granules have an average diameter of 3mm and no pre-treatment process was carried. N_2 flow rate used in this study was varied 400 mL/min., 500 mL/min., and 600 mL/min. Each flow rate involved variation of feed compositions of 0%, 50%, and 100% by weight of PP plastic. The reactor design of co-pyrolysis used in this study is shown in Figure 1. The reactor was of cylindrical shape with diameter of 94mm and aspect ratio (height to diameter ratio) of 1.3.

During this study a total feed mass of 100 grams was fed to the stirred tank reactor at a heating rate of 5ºC/min until the final temperature reached 500ºC, with a holding time of 10 minutes at 500ºC. The stirrer speed used was 60 rpm. The condensable gas product was condensed in a series of two bulb condensers using cooling water and then the bio-oil product was collected in an Erlenmeyer. The cooling water used had a temperature of 15ºC. At the end of each run, the liquid product was weighed, separated polar phase bio-oil and nonpolar phase bio-oil were analyzed using FTIR, GC-MS, H-NMR characterization.

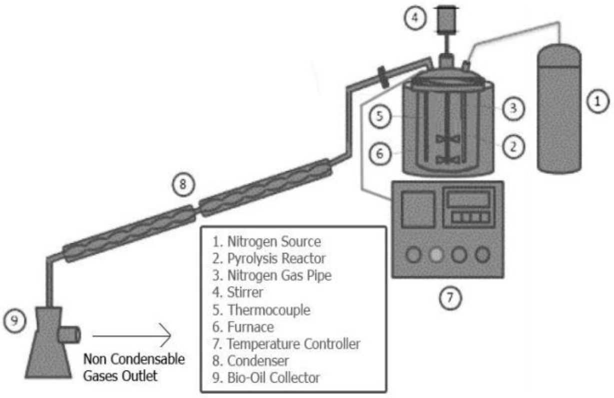

Figure 1. Reactor of co-pyrolysis of corncob and PP plastic and its auxiliries[4)].

3. Results and Discussion

3.1 Yields of Slow Co-Pyrolysis Products

The results of the pyrolysis process that has been carried out on each independent variable produce bio-oil, wax, char and non-condensable gas products. Each yield of each product from pyrolysis in this study is shown in Table 1

Table 1. Yields of slow co-pyrolysis products

N_2 Flow Rate (mL/min.)	Mass Feed (gram)		Bio-Oil (gram)	Char (gram)
	PP	biomass		
400	50	50	44.2	18
500	50	50	45	16
600	50	50	47.9	15
400	100	0	78.7	0
500	100	0	79	0
600	100	0	80.4	0
400	0	100	30.9	34
500	0	100	32.3	31.7
600	0	100	32.79	30

Table 1 shows that at lower N_2 gas flow rate, the bio-oil product decreased, whereas the resulting char increased. This seems to be associated with more local turbulence as the flow of N_2 was increased[10]. More mixing intensity was expected to improve heat convective heat transfer and consequently feed interaction and co-pyrolysis. Convective heat transfer may have occurred where biomass particles immersed in melted PP. With impeller rotation speed of 60 rpm and the reactor diameter of 94 mm in the present work, the tangential velocity on the inner wall of the reactor was estimated 0.29 m/sec. According to Sato et al[11]), the minimum velocity of melted PP on a hot solid surface to induce convective heat transfer to melted PP at temperatures between 200 to 250°C is 0.078 mm/sec. In comparison, the tangential velocity in the present work, i.e. 0.29 m/sec, was much higher than 0.078 mm/sec. Sato et al[11]) found that at this high tangential velocity, the convective heat transfer coefficient was predominant. The hydrogen transfer became more effective to improve interaction between hydroxyl radicals from biomass pyrolysis and H radicals from PP pyrolysis to selectively form more bio-oil and inhibit char formation [12]). Figure 2a shows that there was a synergistic effect on the yield of non-polar fraction of bio-oil as co-pyrolysis was carried out. It can be seen by comparing the nonpolar bio-oil volumes produced from the experiment against that of obtained theoretically (calculated proportionally based on non-polar volume obtained from pyrolysis at 0 and 100%PP).

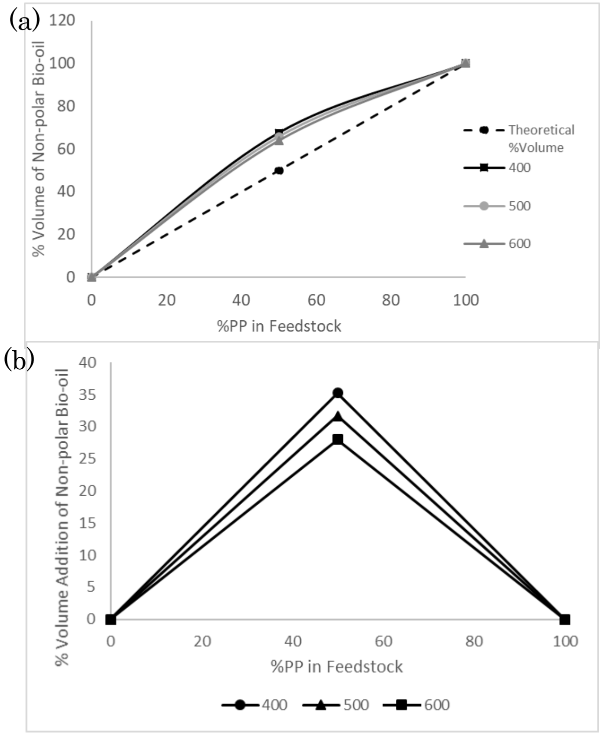

Figure 2. (a) % volume of nonpolar bio-oil (b) % volume addition of nonpolar bio-oil at different N_2 flowrates (mL/min)

Based on Figure 2b, quantitatively it can be concluded that there was an increase in volume at each variation of the N_2 flow rate. The highest synergistic effect produced at a flow rate of 400 mL/min., i.e. 35% non-polar phase addition. Synergistic effects occurred due to thermal co-pyrolysis mechanism which started from pyrolysis of lignin of biomass, oxygenated free radicals released by lignin to plastic and hydrogen radicals released due plastic decomposition, so that H transfers occurred to biomass. The presence of biomass free radicals helped the plastic cracking process, so long plastic chains will be depolymerized and cleaved to produce hydrogen radicals in the process[13]).

3.2 Characterization of Non Polar Fraction of Bio-Oil

Nonpolar phase of bio-oil was produced by pyrolysis using 100% PP plastic feed and 50% PP plastic feed. Characterization of nonpolar phase of bio-oil used FTIR, GC-MS and H-NMR. FTIR characterization of non-polar phase from pyrolysis with a feed composition of 50% PP plastic, and 100% PP plastic are shown in Figure 3. Based on Figure 3. it was concluded that both phases at various N_2 flow rates had a similar spectrum tendency with strong absorbance at wave number 2913 cm^{-1}, 2871 cm^{-1}, 2842 cm^{-1}, 1456 cm^{-1}, 1376 cm^{-1}, and 886 cm^{-1}. The strong wave numbers identify the existence of an aliphatic group shown by the presence of C-H stretch of alkane methyl (2970 - 2950 cm^{-1} and 2880-2860 cm^{-1}), C=C alkene stretch (1613-1450 cm^{-1}) and C-C stretch (400-900 cm^{-1}). The presence of alkane and alkene compounds identified in FTIR analysis is supported by the GC-MS characterization results in Figure 4.

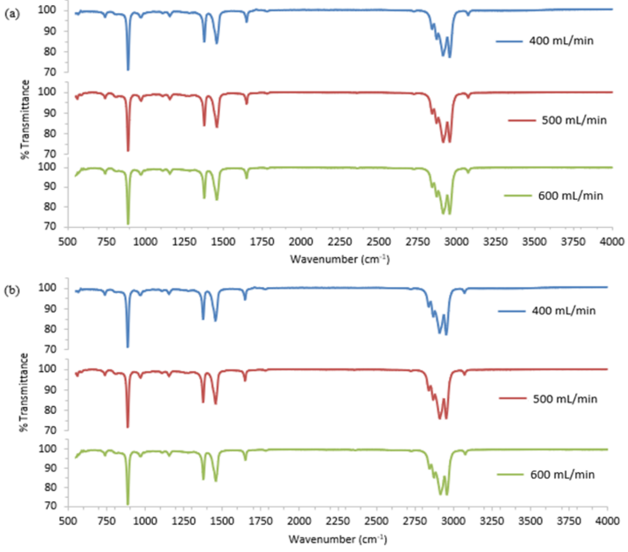

Figure 3. FTIR analysis results of non-polar fraction of bio-oil (a) 50% PP plastic feed, (b) 100% PP plastic feed at different N_2 flowrates (mL/min)

Figure 4 shows that in light bio-oil, both phases exhibited similar trend, where alkenes were predominant carbon chain, followed by alkanes and cycloalkanes. However, co-pyrolysis produced more composition of alkenes. This shows that co-pyrolysis pushed more to the cracking of PP molecules, which was caused by the interaction of free radicals from biomass and PP plastic[11]. Figure 4 also shows that by increasing N_2 flow, alkenes were more generated, while alkanes reduced. As explained previously, the more local turbulence created by higher N_2 flow rate improved the convective heat transfer and consequently more cracking of PP compounds and more alkenes generated[14].

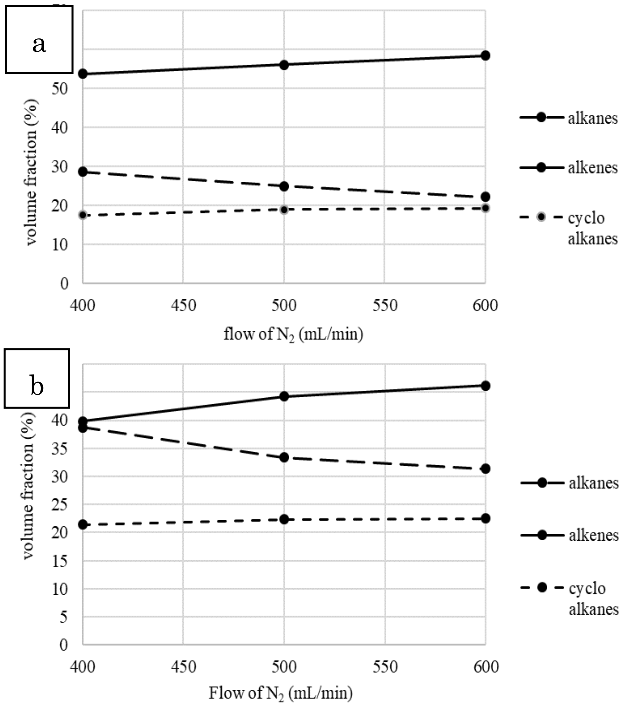

Figure 4. GC-MS analysis results of non-polar bio-oil (a) 50% PP plastic feed, (b) 100% PP plastic feed

LC-MS analysis results of non-polar fraction of bio-oil at various N_2 gas flow rates obtained from pyrolysis with 100% PP plastic feed are shown on Figure 5. It can be seen that at 50% PP feed, pyrolysis resulted in sharp molecular weight distribution where it contained low moles at low molecular weight and high moles at high molecular weight. Comparison between Figures 5a and 5b indicates that there was shifting of molecular weight towards higher molecular weight as result of co-pyrolysis. Therefore, radical interaction during co-pyrolysis improved carbon chain length[11].

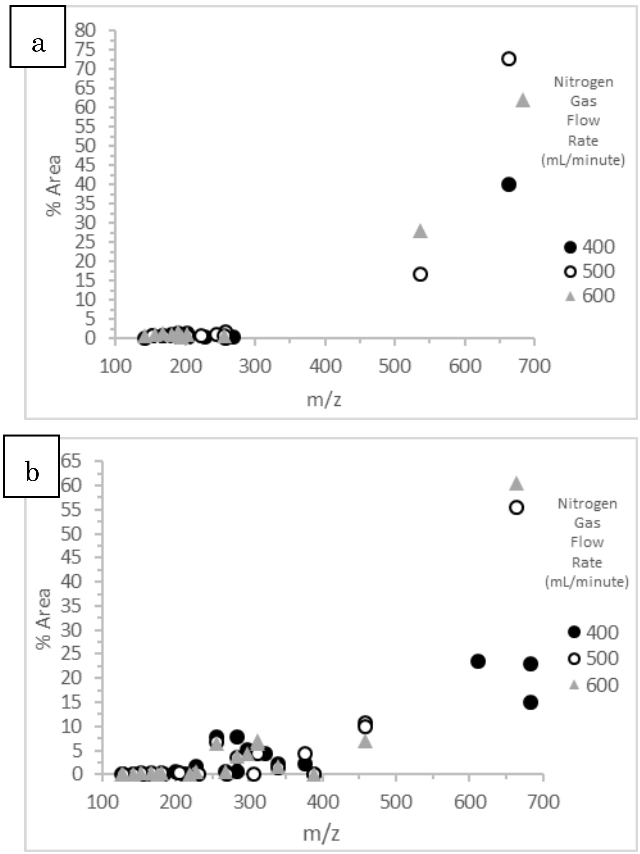

Figure 5. LC-MS analysis result of non-polar bio-oil (a) 50% PP plastic feed, (b) 100% PP plastic feed

The results of H-NMR characterization on non-polar phase from pyrolysis with 50% PP plastic feed are shown in Table 2., while the results of the H-NMR of non-polar of bio-oil from pyrolysis of pure PP plastic are shown in Table 3. H-NMR analysis results show that nonpolar phase obtained from pyrolysis with 50% PP plastic and 100% PP plastic feeds had similar characteristics in which methyl group was dominant and alkene content was about 6-7%. In the case of the effect of N_2 gas flow rate, the tables show that greater N_2 flow rate produced more alkenes. This result is consistent with the trend exhibited by GC-MS characterization under similar conditions. However, in terms of composition comparison, alkene composition measured by H-NMR was low, while by GC-MS was high. This difference arises due to restricted capability of GC-MS of determining composition only to low molecular weight compounds[15]. From this comparison, it can be suggested that double bonds mostly adhered to small compounds, while alkanes were present in various carbon chain sizes.

Branching index (*BI*) is calculated using formula proposed by Yan et al.[16]:

$$BI = \frac{\left[\left(\frac{1}{3}\right)S_{CH_3}\right]}{\left(\frac{1}{2}\right)(S_{CH_2}+S_{CH})} \tag{1}$$

where S_{CH_3}, S_{CH_2} and S_{CH} are % amount of protons in CH_3, CH_2 and CH, respectively.

Table 2. H-NMR results of non-polar phase from pyrolysis with 50% PP feed

Composition of PP (%wt)	50%		
Flow of N_2 (mL/min.)	400	500	600
%H at vinylic C	6.18	6.27	6.89
%H at allylic C	5.44	5.59	6.02
%H at methine	23.72	23.87	24.00
%H at methylene	11.58	12.29	12.87
%H at methyl	53.08	51.98	50.22
Branching Index	1.00	0.96	0.90

Table 3. H-NMR results of non-polar phase from pyrolysis with 100% PP feed

Composition of PP (%wt)	100%		
Flow of N_2 (mL/min.)	400	500	600
%H at vinylic C	6.33	6.55	7.23
%H at allylic C	4.25	5.01	5.33
%H at methine	21.74	22.86	23.12
%H at methylene	11.31	12.68	13.54
%H at methyl	56.38	52.90	50.78
Branching Index	1.14	0.99	0.92

Data in Tables 2 and 3 shows that the greater the N_2 flow rate, the smaller was the BI value. The smaller BI indicates that bio-oil contained longer carbon chains or more molecular weight compounds16). This occurred because at a higher flow rate there would be a shorter time for pyrolysis to preserve cracking to form smaller molecules17). Tables 2 and 3 shows that BI of non-polar phase were in the range of 0.9 – 1.14. By comparison, BI of commercial diesel fuel is about 0.618). Therefore, there is still large difference between BI of bio-oil and that of commercial diesel. To upgrade into biofuel, non-polar phase of bio-oil needs to modify small molecules into longer molecules and reduce the content of alkenes. Small molecules were present as a result of biomass pyrolysis11). To be used as diesel fuel, the alkene content in non-polar phase should be reduced significantly because double bonds are not favorable during combustion as polymerization easily occurred19).

3.3 Characterization of Polar Fraction of Bio-Oil

Polar phases of bio-oil were produced from pyrolysis using 100% corncob and 50% PP plastic feeds. Characterization of polar phase used FTIR and GC-MS analysis (see Figures 6 and 7). Based on Figure 6, it can be concluded that the polar phases of bio-oil obtained from pyrolysis using 50% PP plastic and 100% corncob feeds had similar FTIR spectra even though they produced under different N_2 flow rates with strong absorbance at wave numbers 3364 cm^{-1}, 1708 cm^{-1}, 1384 cm^{-1}, and 625 cm^{-1}. The strongest spectra were at wave number of 3364 cm^{-1}. It identified chemical bonds O-H stretch (3570-3200 cm^{-1}) in carbohydrate compounds. At wave number 1735 cm-1 was C=O stretch on the carbonyl group (1733-1741 cm^{-1}) which identifies carboxylic groups from pyrolysis of cellulose and hemicellulose, and waves of 641 cm^{-1} is CH bend in aromatics (920 -590 cm^{-1}) which identifies aromatic-OH compounds such as phenol from pyrolysis of cellulose, and hemicellulose. FTIR characterization are supported by the GC-MS characterization results in Figure 7.

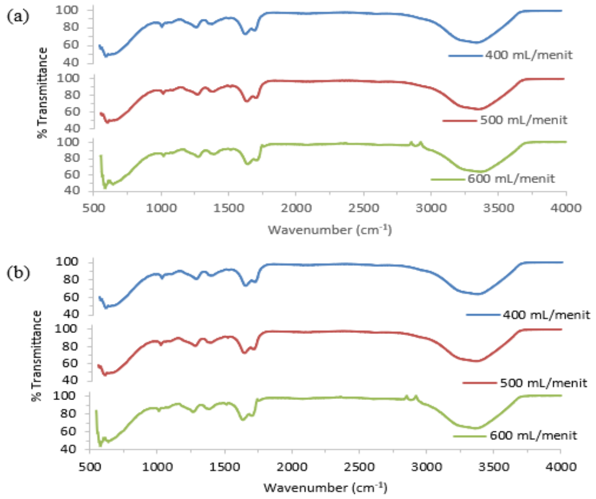

Figure 6. The FTIR results of polar bio-oil (a) 50% corn cob feed, (b) 100% corn cob feed at different N_2 gas flows

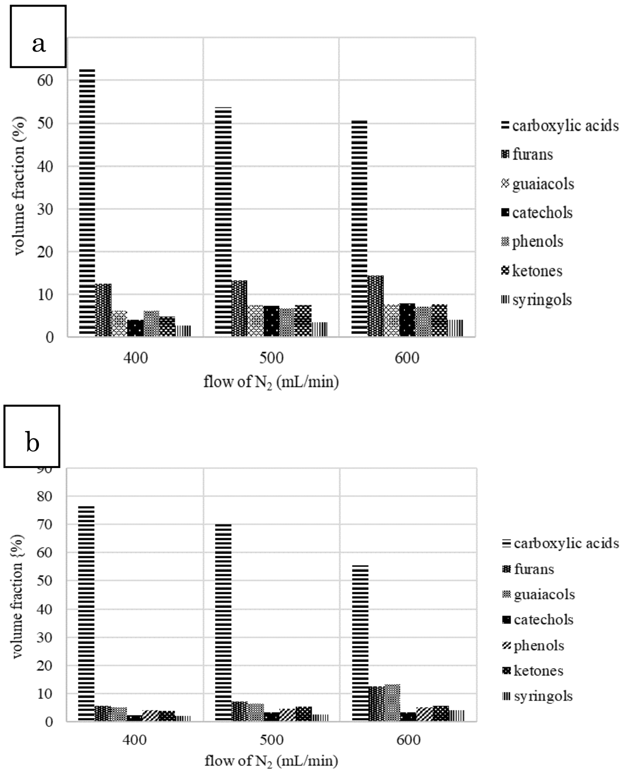

Figure 7. GC-MS analysis results of non-polar bio-oil (a) 50% corn cob feed, (b) 100% corn cob feed

GC-MS analysis of polar phase of bio-oil from pyrolysis with 100% and 50% corncob feeds produce similar trends for carboxylic acids. Based on Fig 7, it can be suggested that at higher N_2 flow rate the composition of the carboxylic functional group dominated by acetic acid decreased, while the compositions of phenolics (containing guaiacol, catechol, phenol, syringol) and ketone compounds increased.

Huang et al[20], found that acetic acid was mostly formed from pyrolysis of O-acetylxylopyranose and it occurred during primary pyrolysis so that its presence depended on residence time offered by N_2 flow. Therefore, the higher N_2 flow, which was shorter residence time, the yield of acetic acid reduced. The formation of furans occurred concurrently with the formation of acetic acid and their selectivity then depended on the selectivity to form acetic acid[21]. Consequently, when the N_2 flow rate was greater, the composition of furan functional groups would increase. Furan aromatic compounds are derived compounds from cellulose and hemicellulose decomposition[22]. The formation of phenolic compounds (phenol, guaiacols, catechols, and syringols) depended on how flow of N_2 affected the char formation, because the char is generated by aromatic ring deposition. By increasing flow of N_2 flow, turbulence induced more H abstraction from PP radicals by biomass radicals increased which retarded repolymerisation of phenolics to form char[23]. Therefore, in Figure 7a, increasing flow of N_2 increased compositions of phenolics. In the case of pyrolysis of pure biomass (see Figure 7b), the compositions of phenolics were smaller than those obtained from co-pyrolysis as a result of hydrogen deficiency in biomass pyrolysis. This condition favored more char production, thus reducing phenolic composition in bio-oil.

Based on Figures 8a and 8b, it can be concluded that polar bio-oil in average had a large molecular weight. At 50% PP feed composition, high molecular weight distribution tended to be narrower compared to that obtained from 100% biomass. High interaction between free radicals of biomass and plastic in co-pyrolysis allowed hydrogen radicals from PP pyrolysis to crack and stabilize biomass radicals[23] resulting in narrower high molecular weight distribution.

The results of H-NMR characterization of polar phase of bio-oil obtained from pyrolysis using 50% corncob feed are shown in Table 4., while those using 100% corn cobs are shown in Table 5. In terms of the trend of compositions of acetic acid and cyclic products (furans and phenolic derivatives) under the influence of N_2 flow, H-NMR and GC-MS give similar results. However, they present different results in terms of the magnitude of compositions, in which carbohydrates became major components in bio-oil measured by H-NMR, while in GC-MS measurement, acetic acid was the main component.

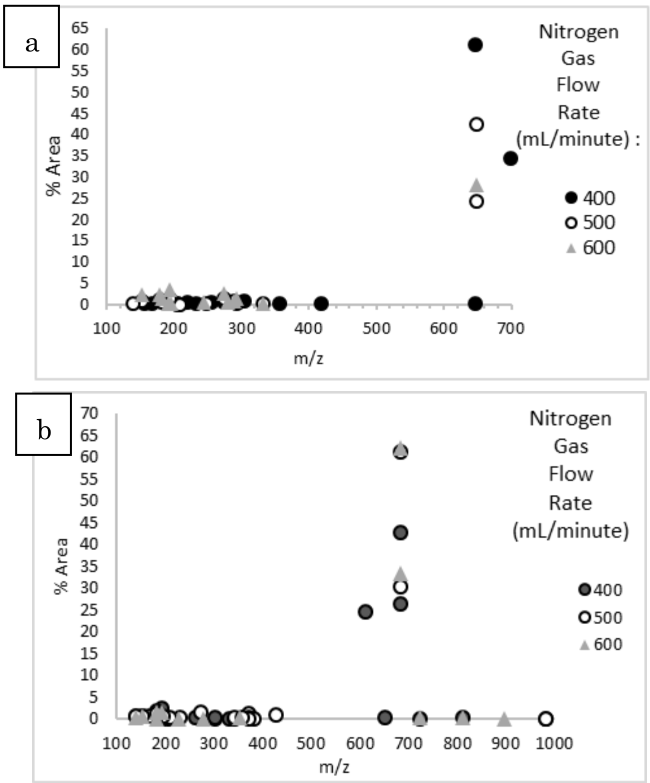

Figure 8. LC-MS analysis results of non-polar bio-oil (a) 50% corn cob feed, (b) 100% corn cob feed

Table 4. H-NMR results of polar phase from pyrolysis with 50% corn cob feed

Composition of Corn Cobs (%wt)	50%		
N_2 flow rate (mL/min.)	400	500	600
%H at C=O of aldehydes	1.01	0.09	0.08
%H at ring of furans	0.20	0.34	0.44
%H at ring of phenolics	1.02	1.33	1.44
%H at OH of carbohydrates	84.81	89.83	93.12
%H at C-alpha of carbonyl	11.67	7.72	4.30
% H of methyl	1.28	0.70	0.63

Table 5. H-NMR results of polar phase from pyrolysis with 100% corn cob feed

Compositions of Corn Cobs (%wt)	100%		
N_2 flow rate (mL/min.)	400	500	600
%H at C=O of aldehydes	0.06	0.52	0.06
%H at ring of furans	0.57	0.84	0.93
%H at ring of phenolics	10.08	12.16	10.08
%H at OH of carbohydrates	79.59	79.45	82.23
%H at C-alpha of carbonyl	8.58	5.28	5.09
% H of methyl	1.12	1.05	0.72

Based on Table 4 and Table 5, it indicates that carbohydrates detected as macromolecules, which were not detected by GC-MS analysis. Moreover, the presence of carbohydrates indicates that biomass pyrolysis did not completely decompose cellulose and hemicellulose to form light molecule oxygenates24)25). This suggests that at N_2 flow applied, the height of the reactor was not high enough to accommodate secondary pyrolysis to form light oxygenated compounds24)25). Comparison of compositions of phenolics in Tables 4 and 5 shows that co-pyrolysis reduced their composition. It seems that biomass pyrolysis had more severity towards the decompositions of cellulose and hemicellulose compared to co-pyrolysis resulting in less carbohydrate, aldehyde and carboxylic acid compositions in bio-oil produced by biomass pyrolysis.

4. Conclusions

The conclusions that can be drawn from the present study of co-pyrolysis of corn cobs and PP are as follows:

1. The higher the N_2 gas flow rate resulted in higher bio-oil yield and lower yield char.
2. Co-pyrolysis favored synergistic effect on non-polar phase yield and lower N_2 flow resulted in more synergistic effect. The maximum non-polar fraction addition from its theoretical fraction in bio-oil was 35%.
3. GC-MS which exhibited composition in light fraction of bio-oil and H-NMR analysis which exhibited bio-oil composition as a whole demonstrate different results. For non-polar phase of bio-oil, GC-MS analysis shows the dominance of alkenes in light fraction of bio-oil, while H-NMR shows the dominance of methyl in bio-oil with double bonds of alkene content 6-7% mole. For polar phase of bio-oil, GC-MS analysis shows the dominance of carboxylic acids in light fraction of bio-oil, while H-NMR shows the dominance of carbohydrates in bio-oil.
4. H-NMR analysis shows that for non-polar phase of bio-oil, increasing flow of N_2 gas increased the composition of alkenes, but reduced that of methyl, while for polar-phase of bio-oil, increasing flow of N_2 reduced the composition of carboxylic acids, but increased that of carbohydrates
5. To utilize non-polar phase of bio-oil as biodiesel, branching index needs to be reduced about one third to a half and alkene content needs to be decreased
6. Co-pyrolysis allows diminishing phenolic content in polar phase of bio-oil which increased the dominance of carbohydrate in the polar phase.

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