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Characteristics of Non-Polar Bio-oil Produced by Co-pyrolysis of Corn Cobs and Polypropylene using CO₂ as Carrier Gas

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CO₂ is chosen to substitute N₂ as a carrier gas in biomass-polypropylene (PP) pyrolysis due to its abundant availability at low cost and favourable heat emissivity. There has been no research on co-pyrolysis utilising CO₂ gas as sweep gas to bring co-pyrolysis vapour out of the pyrolysis reactor. The objective of the present research is to investigate effect of the use of CO₂ as gas carrier on bio-oil yield in comparison to the use of N₂ and on compositions of the resulting non-polar fraction of the bio-oil. Polypropylene composition in the feed was varied 0, 25, 50, 75, and 100 weight %. The co-pyrolysis was conducted in a stirred tank reactor at heating rate of 5°C/min and maximum temperature of 500°C. Yield of non-polar fraction of bio-oil was more dependent to the type of carrier gas than the yield of polar fraction. Synergistic effect on non-polar of bio-oil obtained from co-pyrolysis in CO₂ environment was achieved as the PP composition in feeds more than 40%. H-NMR analysis suggest that in the whole content of non-polar fraction obtained from co-pyrolysis, the compositions of alkenes were low about 6% with the rest mostly alkanes independent of PP composition in feed. However, their branching indices were still about 2.5 times higher than that of diesel fuel advocating the need of adjustment in carbon- chain structure in the non-polar fraction of bio-oil to attain less branching of methyl

Keywords: Co-pyrolysis; Corn cobs; Polypropylene; Carrier Gas; Carbon Dioxide; Bio-oil.

1. Introduction

Energy security has become a global concern and has been delivered at many world forums and top-level conferences¹⁾. The depletion of fossil fuels and the environmental damage caused by fossil fuel usage have encouraged research in the field of renewable energy. Particularly, one of the most established sub-division of renewable energy research is the synthesis of liquid bio-oil from various methods and raw materials. Bio-oil is a promising substance that could be a future substitute of liquid fossil fuel for transportation and electricity generation.

One of the most studied methods of bio-oil production is co-pyrolysis of biomass and plastics. Co-pyrolysis produces non-condensable gas, liquid bio-oil and char. 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 plastics²⁾. The presence of plastic in co-pyrolysis will reduce the oxygen content in bio-oil. Although very promising, the resulting bio-oil has a low calorific value, high degree of

corrosiveness and chemical instability caused by remaining oxygenate in bio-oil³⁾. It is therefore important to separate bio-oil into two different fractions; non-polar fraction, which can be further processed into bio-fuel, and the polar fraction.

A study by Supramono et al.⁴⁾ shows an occurrence of synergistic effect in slow co-pyrolysis of corn cobs and polypropylene (PP) in a stirred tank reactor with N₂ as a carrier gas. The experiment was conducted in a slow heating rate of 5°C/min. until all the substances in the reactor reached 500°C. The synergistic effect includes a higher resulting yield of bio-oil compared to that of the combined bio-oil produced by pyrolysis of pure biomass and pure PP. Other than that, it is shown that the same experiment arrangement promotes the reduction of oxygenated compound content in the bio-oil, which is promoted by introduction of hydrogen radicals donated by PP pyrolysis that substitute oxygen in bio-oil molecules. The stirred tank reactor configuration allows phase separation between polar and non-polar compounds of bio-oil caused by asymmetric viscosity between the two and by average low viscosity. This low viscosity is

achieved as a result of enhanced convection heat transfer due to the presence of N₂ bubble turbulence in the plastic melt⁵). The non-polar fraction of bio-oil then could be upgraded to be used as bio-fuel.

The use of N₂ as carrier gas is predicted to have a negative economic effect for the scale-up of bio-oil production in a stirred tank reactor configuration due to its high price compared to other available industrial gases⁶). Therefore, it is proposed to substitute N₂ with a cheaper gas, such as CO₂. Besides its lower price and wider availability, CO₂ is known to have a greenhouse effect because of its high emissivity⁷), thus enhancing the heat flux from the reactor wall to the feed mixture. Other well-known effect includes chemical interaction between CO₂ and reactant in a high temperature environment⁸). In authors' knowledge, there has been no research concerning the use of CO₂ as a carrier gas in co-pyrolysis.

In the present study, bio-oil synthesis from corn cobs and PP in a stirred tank reactor is conducted using CO₂ as carrier gas. The aim of the present study is to investigate effect of the use of CO₂ gas as a carrier gas on the yield of non-polar fraction of bio-oil in co-pyrolysis biomass-plastic polymer and on its chemical composition. It is predicted that CO₂ will affect the yield of products and bio-oil composition, both in non-polar and polar fractions.

2. Materials and Methods

2.1. Materials

Corn cob particles were bought from East Java, Indonesia. PP plastic beads were bought from a chemical company in Banten, Indonesia. N₂ and CO₂ gases were bought from a gas company, PT Samator Gas Industri.

2.2. Method

Corn cob particles were sieved until their size reached 8-20 mesh and then dried to reach moisture content to maximum 10%. Bio-oil synthesis was conducted by co-pyrolysing treated corn cobs with PP beads in a stirred tank reactor. The co-pyrolysis process was conducted with a low heating rate (5°C/minute) and stirrer rotational speed of 100 rpm. Carbon dioxide (CO₂) and nitrogen (N₂) gases were used as carrier gases with flow rate of 750 mL/minute. The feed composition ratio for the co-pyrolysis process of corn-cobs to PP was 0%:100%, 25%:75%, 50%:50%, 75%:25% and 100%:0% mass. Two series bulb condensers were used to condense resulting organic vapour into bio-oil with cooling water temperature of 10-15°C. Figure 1 shows a schematic diagram of the apparatus used on the bio-oil synthesis.

The use of stirred tank reactor at low heating rate is beneficial because bio-oil separates into 2-phases, with upper layer containing non-polar (non-oxygenated) components and lower layer polar (oxygenated) components. This allows hydrogenation in the next step to be applied only on non-oxygenated fraction of bio-oil to

form bio-fuel.

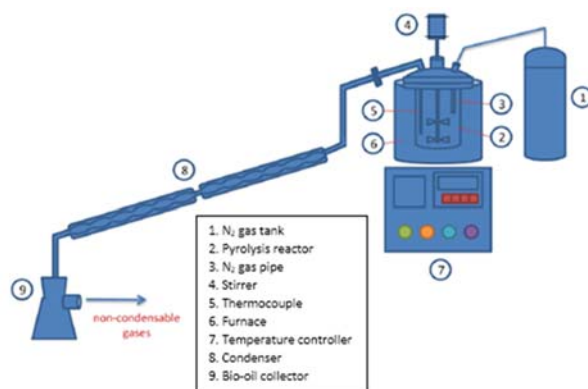


Figure 1. Schematic diagram of co-pyrolysis apparatus⁵)

3. Result and Discussion

3.1 Yields of Co-Pyrolysis Products

Yields of pyrolysis products, i.e. bio-oil, wax, and char from pyrolysis using CO₂ and N₂ atmosphere are shown in Figures 2, 3 and 4. respectively.

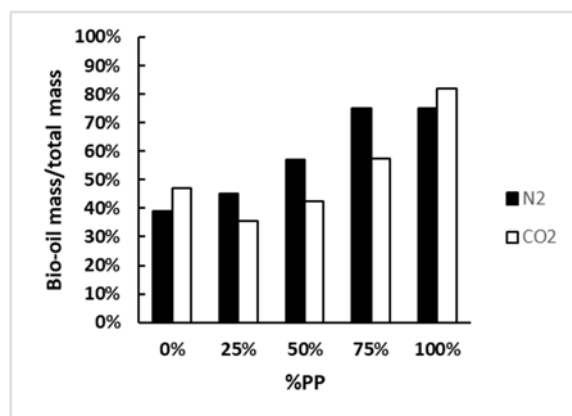


Figure 2. Comparison of bio-oil yields using carrier gases N₂ and CO₂ at various PP compositions

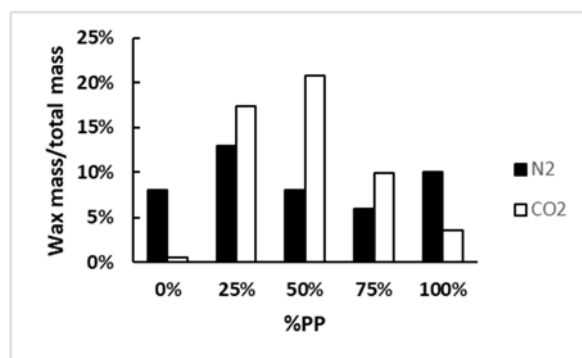


Figure 3. Comparison of wax yields using carrier gases N₂ and CO₂ at various PP compositions

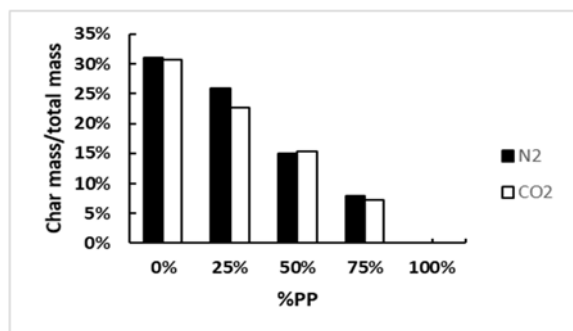


Figure 4. Comparison of char yields using carrier gases N₂ and CO₂ at various PP compositions

In CO₂ atmosphere, one should see differences in bio-oil yields depending on feed conditions, i.e. pure corn cobs, pure PP beads, and mixed feed. When pure feed was used, bio-oil yields were higher and wax yields were lower in CO₂ atmosphere compared to those in N₂ atmosphere. These facts related to biomass pyrolysis are similar to those measured by Yang et al.⁹ who worked on biomass fast pyrolysis. Experiment of biomass pyrolysis at temperatures of 300, 400 and 500°C by Pilon and Lavoie¹⁰ implies that in biomass pyrolysis using CO₂ as carrier gas, CO₂ is chemically not involved in the pyrolysis reactions. Therefore, its role in pyrolysis was to improve heat transfer in pyrolysis. This arises due to higher emissivity of CO₂ compared to N₂ which exerts higher heat flux. The effect of the use of different carrier gases on biomass pyrolysis yields may be analogous to the pyrolysis of using slightly different heating rates which contributes different heat fluxes. Some researchers found that higher heat flux on biomass enhanced decomposition of biomass towards bio-oil. Haykiri-Acma et al.¹¹ noted that pyrolysis of biomass at heating rates varied from 5 to 50°C/min results in higher yield of bio-oil at higher heating rate. Pei et al.¹² found in the pyrolysis of three typical plastics, polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) using 4 different low heating rates, i.e. 3.7, 9.0, 20.6 and 33.3°C/min that increasing heating rate improves the yield of oil and reduces that of non-condensable gas.

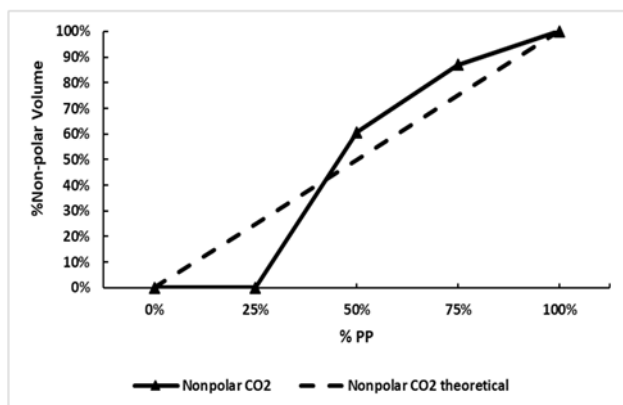


Figure 5. Volume fraction of non-polar phase and its theoretical value at various PP compositions in CO₂ atmosphere

When mixed feed composition was used, bio-oil yields were lower and wax yields higher in CO₂ atmosphere compared to those in N₂ atmosphere, as can be seen in Figures 2 and 3. In this case, higher emissivity of CO₂ gas improved both PP and biomass extent of pyrolysis which reduced char pyrolysis slightly (see Figure 4) and intensified PP pyrolysis to produce low molecular weight hydrocarbon compounds. It seems that low molecular weight compounds from PP pyrolysis repolymerised to form wax¹³, in which co-pyrolysis using CO₂ gave higher yield of wax those using N₂ gas (see Figure 3). Comparing Figure 3, which is attributed to PP pyrolysis, and Figure 4, which is attributed to biomass pyrolysis¹⁴, it is inferred that biomass was much less sensitive to the change of heat flux as N₂ gas was replaced by CO₂ gas.

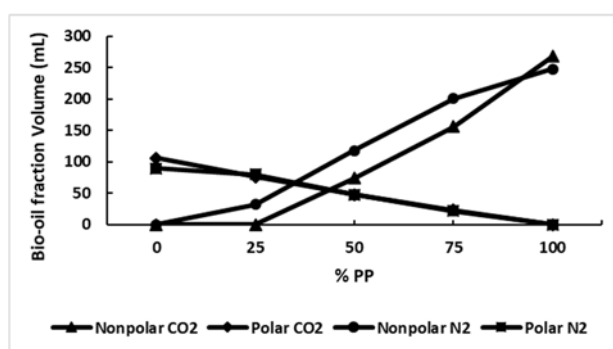


Figure 6. Volume fractions of polar and non-polar phases of bio-oil in N₂ and CO₂ atmospheres at various PP compositions

Figure 5 shows the actual non-polar volume fractions of bio-oil in CO₂ atmosphere compared to their theoretical volume fractions calculated proportional to its fractions at biomass and PP pyrolysis starting from feed containing about 40%PP. The figure shows that there has been a synergistic effect on the non-polar phase of bio-oil even though the use of CO₂ gas has dropped the yield of bio-oil compared to the use of N₂ gas as described by Figure 2. This indicates that free radicals of PP pyrolysis in CO₂ environment were still capable of transferring hydrogen to free radicals which improved contents of hydrogen and carbon in bio-oil to form non-oxygenated (non-polar) phase¹⁵.

However, using feeds containing less than 40% weight of PP, Figure 5 shows that there was negative synergistic effect on non-polar phase yield and co-pyrolysis lost its non-polar yield at the feed composition of 25% PP. In this regime, high composition of OH radicals as strong oxidising agents was produced by cellulose and hemicellulose pyrolysis¹⁶. Co-pyrolysis worked in coincide with oxidation reactions of PP and produced crosslinking of PP leading to char formation¹⁷.

Figure 6 shows that volumes of polar fractions obtained from co-pyrolysis in CO₂ environment were very similar to those in N₂ environment. This indicates that even though bio-oil yields produced in co-pyrolysis in CO₂

environment were lower than those in N_2 environment as described by Figure 2, additional heat flux by CO_2 gas radiation improved the pyrolysis of biomass to form polar fraction than attained in N_2 environment. At low PP composition in feeds, some of biomass particles submerged in PP melt, while rest were blanketed by thin film of PP melt. In this case, some of biomass particles were heat radiated by the hot reactor wall through thin film of PP melt. The film was transparent to the heat radiation¹⁸. At high PP composition of feeds, all biomass particles submerged in thick PP melt and in stirring, there was heat convection from the hot reactor wall through PP melt to biomass particles¹⁹. In this regime where PP compositions started to exceed biomass compositions in feeds, the heat radiation enhanced by CO_2 gas carrier worked with partial transparency of PP²⁰. The high emissivity of CO_2 gas enhanced the primary and secondary pyrolysis of biomass where most of cellulose and hemicellulose decomposition occurred between 270

to $320^\circ C$ ²¹) and high mass decomposition of PP occurred above $400^\circ C$ ²²). These mass decomposition data indicate that biomass particles were still blanketed with PP melt when most of cellulose and hemicellulose were pyrolysed.

Figure 6 also shows that volumes of nonpolar fractions obtained from co-pyrolysis in CO_2 environment were lower than those in N_2 environment. Nonpolar fraction mostly originated from PP pyrolysis with some fraction originated from biomass pyrolysis as a result of hydrogen abstraction by free radicals of PP to those of biomass PP¹⁴. With long residence time in the present reactor, PP compounds which contained high proportion of tertiary carbon and branching structures are easily degraded in vapour phase^{23,24}. Again, high emissivity of CO_2 allowed further cracking of PP resulting in reduced non-polar fraction of bio-oil yield and increased light gas yield.

3.2 Composition of Non Polar Fraction of Bio-Oil

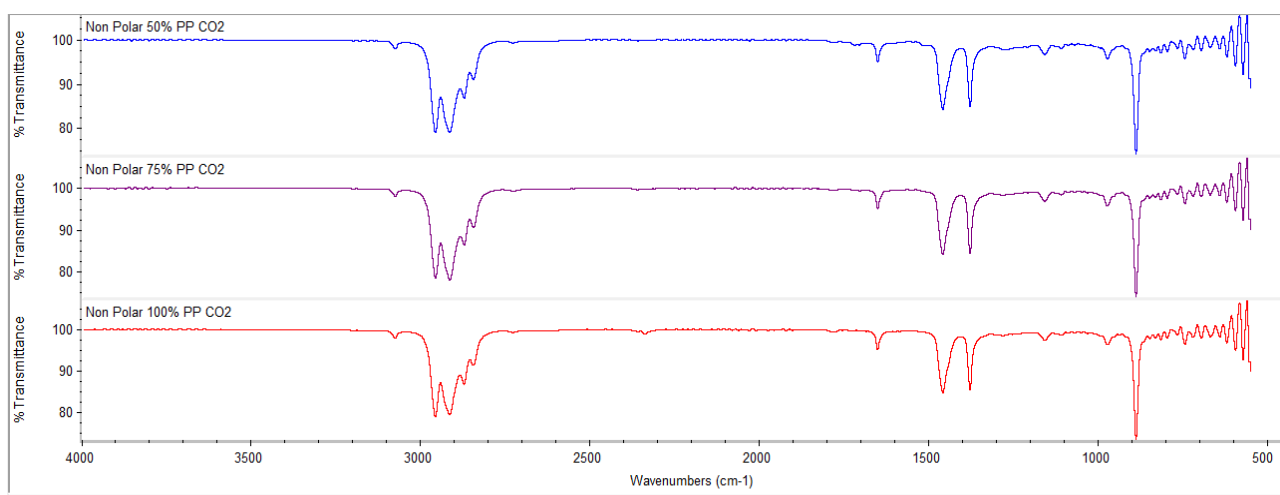


Figure 7. FTIR spectra of non-polar fraction of bio-oil at various PP compositions

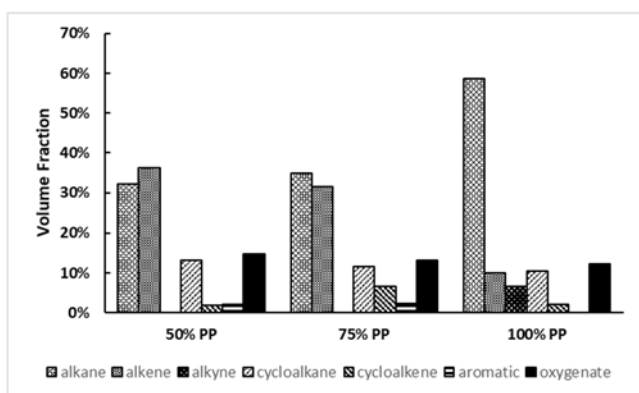


Figure 8. GC-MS analysis of non-polar fraction of bio-oil at various PP compositions

FTIR spectra for non-polar fractions of bio-oil show

the presence of alkane (1,3 *disubstituted*, C-H bending at wave number of 885 cm^{-1} ; *methylene group alkane*, C-H bending 1456 cm^{-1} ; alkane C-H stretching $2840, 2870, 2913\text{ cm}^{-1}$) and alkene (*disubstituted (cis) alkene*, C=C stretching 1650 cm^{-1}) (see Figure 7). The presence of hydroxyl group at wave numbers of 1376 and 3074 cm^{-1} was expectedly due to imperfect separation between non-polar and polar fraction of bio-oil. Three FTIR spectra exhibiting the contents of three non-polar bio-oils attributed to three different feed compositions show no difference between them indicating that co-pyrolysis of different feed compositions exhibited similar non-polar bio-oil chemical chain contents.

GC-MS analysis measuring composition in light fractions of non-polar fractions of bio-oil is shown in Figure 8. It can be seen that fraction of alkanes slightly increased with increasing composition of PP in the feed,

while fraction of alkenes reduced. Biomass contribution to straight-chain alkane is possibly due to degradation of cellulose²⁵). The presence of cycloalkanes and cycloalkanes was observed both in co-pyrolysis and pure PP pyrolysis which indicates that cyclization of plastic oligomers in pure PP pyrolysis also occurred in co-pyrolysis. One of elementary reactions involved in cyclization includes 1,5 or 1,6-cyclisation of the end-chain radicals and subsequent β -scission reactions²⁶) resulting in the presence of oligomers.

H-NMR analysis result for non-polar fractions of bio-oil is shown in Table 1 in which H abundance in allylic bonds was three times that in alkene bonds in co-pyrolysis involving CO₂ gas. By contrast, in co-pyrolysis involving N₂ gas, H abundance in allylic bonds and that in alkene bonds in N₂ atmosphere were similar²⁷). Therefore, the branching in aliphatic structures in non-polar bio-oil obtained by co-pyrolysis in CO₂ is higher than that in N₂ gas. Consequently, non-polar fraction of bio-oil from co-pyrolysis in CO₂ atmosphere is expected to have higher research octane number (RON) compared to that synthesized in N₂ atmosphere.

H-NMR analysis result from diesel fuel shows that diesel fuel has branching index (*BI*) of only 0.4, while non-polar fractions between 1.01 to 1.05. *BI* is calculated using formula proposed by Yan et al.²⁸):

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

where S_{CH_3} , S_{CH_2} and S_{CH} are % amount of protons in CH₃, CH₂ and CH, respectively. It shows that non-polar fraction of bio-oil contained hydrocarbon molecules with larger degree of branching and possible smaller molecular weight distribution compared to commercial diesel fuel²⁹). To upgrade the bio-oil into biofuel, it needs to modify its chemical structure to have lower branching. The introduction of acetylene in PP pyrolysis may be an option to adjust between carbon chain scission and crosslinking to achieve a certain *BI*³⁰).

Table 1. H-NMR analysis of non-polar fraction of bio-oil at various PP compositions

| | 50% PP | 75% PP | 100% PP | Diesel Fuel |
|-------------------------------|--------|--------|---------|-------------|
| %H at methyl | 51.69 | 52.33 | 52.12 | 34.90 |
| %H at methylene | 13.94 | 13.92 | 13.92 | 58.61 |
| %H at methine | 10.09 | 9.61 | 9.61 | 0.00 |
| %H at allylic C | 18.05 | 17.87 | 18.05 | 4.56 |
| % H at vinylic C | 5.98 | 6.12 | 5.87 | 0.00 |
| % H at aromatic ring | 0.13 | 0.12 | 0.09 | 1.93 |
| Branching Index (<i>BI</i>) | 1.01 | 1.05 | 1.05 | 0.40 |

Generally, there was no difference in compositions of

non-polar fractions of bio-oil obtained from different co-pyrolysis feeds detected by H-NMR, in which H-NMR analysed the whole chemical bonds in the bio-oil. This shows that thermochemical mechanisms for non-polar fractions were not different. Differing results of GC-MS from H-NMR analysis are because GC-MS was restricted to detect molecules with molecular weight not more than 550, whose boiling points less the maximum vaporization temperature set up in GC-MS apparatus³¹). Increasing composition of alkanes and decreasing alkene content as detected in GC-MS therefore occurred in the lower molecular weight range. The lower composition of aromatics in H-NMR spectra as opposed to relatively higher content in GC-MS spectra shows that the aromatic compounds were predominant in low molecular weight range.

LC-MS analysis result of non-polar fraction of bio-oil at various PP compositions is shown in Figure 9. From that figure, it can be seen that the range of molecular weight distribution was wider with increasing PP feed composition. At 50% PP feed composition, the range was narrower and has higher maximum %volume than those involving larger PP feed compositions. Interaction between biomass and PP radicals was determined by interaction between H radicals from PP pyrolysis and OH radicals from biomass pyrolysis³²). In excessive H radical environment, H and OH radicals can easily react to form water. This high loss H radical to water affected interaction between biomass radicals and PP radicals. Suriapparao et al.³³) found the presence of OH radicals can reduce the activated energy of PP pyrolysis. Because of reduction of OH radical presence in co-pyrolysis using 75% PP feed, the fragmentation of PP in this co-pyrolysis was less intensive compared to that in co-pyrolysis using 50% PP feed resulting in wide molecular weight range. High intensity of co-pyrolysis using 50%PP feed caused high fragmentation of PP structure resulting high amount of low molecular weight radicals. This also intensified repolymerisation among aliphatic radicals¹³) which culminated as a high maximum %volume of high molecular weight fraction in the co-pyrolysis using 50% PP feed.

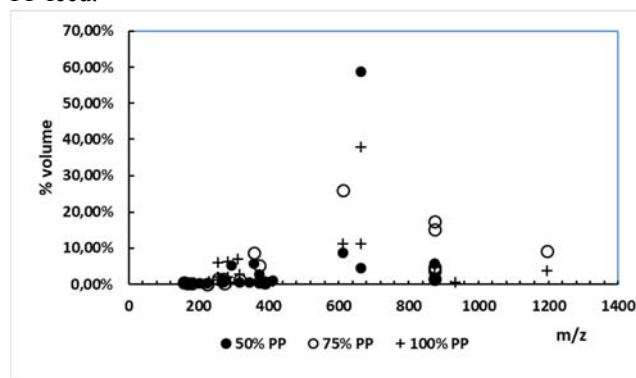


Figure 9. LC-MS analysis of non-polar fraction of bio-oil at various PP compositions

4. Conclusions

The use of CO₂ as carrier gas in co-pyrolysis of corn cobs and PP at low heating rate in comparison to the use of N₂ gas has resulted in higher bio-oil yield for pyrolysis of pure feeds but lower bio-oil yield for co-pyrolysis. The yield of non-polar fraction of bio-oil was more dependent to the use of carrier gas than the yield of polar fraction of bio-oil. Synergistic effect on non-polar fraction for the co-pyrolysis in CO₂ environment occurred as the PP composition in feed more than about 40%. In light fraction of non-polar phase, compositions of alkanes and alkenes were comparable and predominant as the co-pyrolysis used feeds with compositions of PP of 50 and 75%, but the composition of alkanes was predominant as the pyrolysis used pure PP. For the whole content of non-polar fraction of bio-oil, the composition of alkenes was just about 6%. However, the branching indices were still about 2.5 times higher than that of diesel fuel. These high different branching indices advocate the need to make adjustment in carbon- chain structure in the non-polar fraction of bio-oil to attain less branching of methyl.

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