

Co-pyrolysis of corn cobs and polypropylene for production of biofuel similar to gasoline at low heating rate

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Abstract. Co-pyrolysis between corncobs and polypropylene has a synergetic effect that transforms part of polar fraction of bio-oil into non-polar fraction containing non-oxygenate compounds as precursor for synthesis of bio-fuel. In the present work, pyrolysis of the non-polar fraction of bio-oil was led to produce bio-oil with viscosity similar to that of gasoline and contained non-oxygenated compounds. The pyrolysis was carried out in 2 stages, where the first-stage was co-pyrolysis to produce non-polar bio-oil and the second-stage was pyrolysis of non-polar fraction from the first stage to reduce its viscosity similar to that of gasoline. The first and second-stage pyrolysis was carried out in a stirred tank reactor at heating rate of 5°C/min using nitrogen as carrier gas with the second-stage pyrolysis final temperature varied. The resulting bio-oil product was characterized by FT-IR, GC-MS, H-NMR, viscometer and LC-MS. The results show that bio-oil viscosity and yield of the second-stage pyrolysis heavily depended on its final temperature, in which the higher the temperature, the higher was the viscosity, yet the higher was the bio-oil yield. Final temperature of 300°C was the optimal one for obtaining bio-oil similar to gasoline regarding its close viscosity despite of low yield of bio-oil. Pyrolysis of bio-oil may be performed coinciding with attempting of reducing branching index to reduce its viscosity.

1 Introduction

In 2015, Indonesia imported energy around 27% from the total primary energy. The oil production development tends to decrease from 287.30 million barrels to 251.87 million barrels. On the other hand, consumption rate of fuel oil continues to increase. The increase of fuel consumption goes along with economic and population growth whilst the production of raw oil decrease [1].

Corncoobs biomass has a high potential to be developed as a source of bio-oil. There are a lot of corncoobs from maize waste produced by tropical countries. In Indonesia alone, in 2010, the waste produced from maize waste was 17,826 tons [2]. The pyrolysis of corncoobs can produce bio-oils which by hydrogenation process will be able to be used as biofuel either as gasoline or diesel.

Co-pyrolysis between polypropylene plastics and biomass has been researched before and produced low oxygenated bio-oil with higher yields. By using a stirred tank reactor to maximize the heat transfer, the process can be achieved. Co-pyrolysis of polypropylene and corn cobs inside stirred tank reactor also produced two separated phase of bio-oil, in which the top part is a non-oxygenated (non-polar) phase and the bottom phase is an oxygenated (polar) phase [3]. The non-polar phase can

be used as bio-oil as precursor of diesel engine as it does not have any oxygenate compounds [4]. However, the non-polar phase cannot be used as gasoline as its viscosity is much more similar to diesel.

Several works have been performed to produce bio-oil that can be used. Boucher et.al. have done a pyrolysis of softwood bark by adding methanol to achieve bio-oil that can be used as gas turbine fuel [5]. Kumar and Singh pyrolyzed HDPE pellets to achieve bio-oil with kinematic viscosity 3,3 cSt [6]. The viscosity of bio-oil from previous works had been more similar to that of diesel fuel. A research of non-catalytic co-pyrolysis with the purpose of making bio-oil with characteristics close to gasoline is hardly found.

The aim of the present research is to obtain bio-oil that has similar characteristics to gasoline's, so it can be used for internal combustion engines. To produce a bio-oil with viscosity and characteristics similar to gasoline, it has been proposed to do two stages of pyrolysis in a stirred tank reactor. The first-stage pyrolysis produced non-oxygenated bio-oil with viscosity similar to diesel. The second-stage pyrolysis was used to further break down the hydrocarbon chains of the first-stage bio-oil to produce expectedly shorter chains of hydrocarbons.

2 Experimental Setup

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The pyrolysis was carried out in 2 stages, where the first stage was co-pyrolysis of corn cobs and polypropylene to produce non-polar bio-oil and the second stage was pyrolysis of non-polar fraction from the first stage to do more cracking of the first-stage bio-oil product in order to reduce its viscosity leading to that of gasoline. The co-pyrolysis was conducted in a stirred tank reactor with mass composition of corn cobs and polypropylene respectively 12.5% and 87.5% in the feed mixture. Polypropylene was used as a hydrogen donor due to its higher hydrogen to carbon mole ratio compared to that of biomass and can partly provide hydrogen to and partly remove oxygen from biomass pyrolysis products [7]. This allows synergetic effect to produce more non-oxygenated bio-oil by removing oxygen into non-condensable gas composing mostly CO, CO₂ and into bio-oil as H₂O [8]. This feed composition was selected because it produced the highest yield of non-polar bio-oil and the aliphatic composition of the bio-oil was similar to that obtained by co-pyrolysis using any feed mixture containing more than 50% polypropylene [3].

Corn cob particles were obtained from agricultural waste dump in Bogor, Indonesia and sieved to particle sizes of 500µm-1mm. The particles were then dried in an oven to achieve moisture content ≤ 10%. The co-pyrolysis reactor containing corn cob particles and polypropylene granules was heated from ambient temperature to 500°C, with heating rate of 5°C/min and holding time of 10 minutes at constant temperature of 500°C. Nitrogen gas was used as carrier gas. The pyrolytic vapor was condensed with a series of two water-cooled bulb condensers and the bio-oil product were collected in a container. Circulating cooling water at 15°C or less was used for the condensers [9].

The second-stage pyrolysis was conducted in the same reactor with the same conditions except that the final temperature was varied. There were five bio-oil samples obtained from the co-pyrolysis, respectively named as non-polar bio-oil 87.5%PP (a) to (e). Non-polar bio-oil 87.5%PP (a) was used for TGA analysis to get its mass decomposition characteristic. Non-polar bio-oil 87.5%PP (b) to (e) were used as feeds for the second-stage pyrolysis.

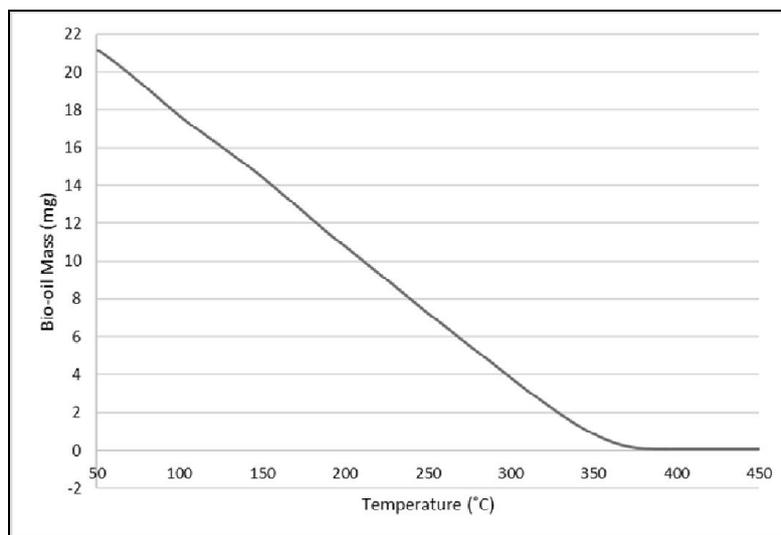


Fig. 1. TGA result of 87.5%PP bio-oil

A 5 ml of the non-polar bio-oil sample were pyrolyzed in a thermogravimetric analyzer (TGA), with the heating rate of 5°C/min until temperature of 600°C. Nitrogen flow used in the TGA was 50 ml/min. The TGA result is exhibited in Fig. 1. The figure implies that the heaviest decomposed mass of the sample under heating rate of 5°C/min evaporated at 375°C. By comparison, the highest boiling point of gasoline is 200°C. It means that the pyrolysis of the bio-oil obtained from the first-stage pyrolysis needs more fragmentation to obtain bio-oil with the heaviest molecules having boiling point about 200°C. Four variations of second-stage pyrolysis final temperatures were selected. i.e. 200°C, 300°C, 375°C and 450°C, which used non-polar bio-oil 87.5%PP (b), (c), (d) and (e) resulting from the first-stage pyrolysis as feeds.

The second-stage pyrolysis was run in a stirred tank reactor and at the same operational conditions for all

feeds, holding time kept for 30 minutes, but the final temperature was varied. The bio-oil samples from the second-stage pyrolysis were then analyzed using viscometer, GC-MS, LC-MS and H-NMR.

The characteristics of bio-oil samples were then compared to gasoline characteristics based on the kinematic viscosity, branching index (BI), and higher heating value (HHV). The branching index was calculated using H-NMR data and by Eq. 1 [10], where S_{CH_3} is the % amount of protons in CH₃ and S_{CH_2+CH} is the sum of % amount of protons in CH₂ and CH. Higher BI value indicates that the carbon chain has more branches [11].

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

Meanwhile the higher heating value was calculated by Eq. 2 [12]. The values of HHV in MJ/kg were also calculated by using H-NMR data.

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (2)$$

where *C*, *H*, *S*, *O*, *N* and *A* were the mass fraction of atoms carbon, hydrogen, sulphur, oxygen, nitrogen and ash, respectively.

3 Results and Discussion

3.1. First-Stage Pyrolysis Bio-oil Characterization

Bio-oil from the first-stage pyrolysis was characterized using FT-IR, GC-MS and H-NMR. The FT-IR result is shown in Fig. 2. The figure shows that the spectra are identical among different products of bio-oil. The main types of carbon chains identified by FTIR were alkanes, alkenes, and cyclohexyl.

To support the FT-IR result, the bio-oil was analyzed by GC-MS to see detailed compound composition. The result is shown in Fig. 3. The type of carbon chain dominating the composition of all bio-oil samples was alkenes. The other carbon chains detected were alkanes, cycloalkanes, cycloalkenes and oxygenates. Due to similarity patterns of FT-IR and GC-MS data among 4 samples of bio-oil, bio-oil obtained from different runs of the first-stage pyrolysis can be considered to have one bio-oil characteristic. This also demonstrates the repeatability of stirred tank reactor results.

The H-NMR result can be seen in the third column of Table 1, where the combined proton composition of methyl, methylene and methyne which represents proton composition in saturated C-C bonds is about 75%. It means that majority of aliphatic groups was of alkanes. This is contrary to the result exhibited by GCMS where the majority of the groups was of alkenes. Sharypov et al [13] and Nanda et al [14] have revealed that GCMS is capable of identifying molecular structures of compounds up to a limited molecular weight. Therefore, data shown in Fig. 3 was restricted to low molecular weight compounds in the bio-oil. GCMS may be able to identify functional groups and types of carbon chains but cannot quantify their compositions in the bio-oil. This result also indicates that alkene compounds may have been mostly as low molecular compounds.

3.2. Second-Stage Pyrolysis Yields

The bio-oil yields in the second-stage pyrolysis are shown in Fig. 4. The bio-oil yield increased as the final temperature of the pyrolysis was increased. This result may be in contrary to what is expected that the higher the final temperature, the lower was the bio-oil yield. The second-stage pyrolysis produced bio-oil which has different characteristics from the bio-oil feed and non-condensable gas. The fashion of Fig. 4 indicates that at higher final temperature, small radicals produced had a tendency to undergo polymerization rather than being combined to produce non-condensable gas. This possibility has also been found by Vinu et al [15]. Indications towards polymerization will be elucidated in following sections.

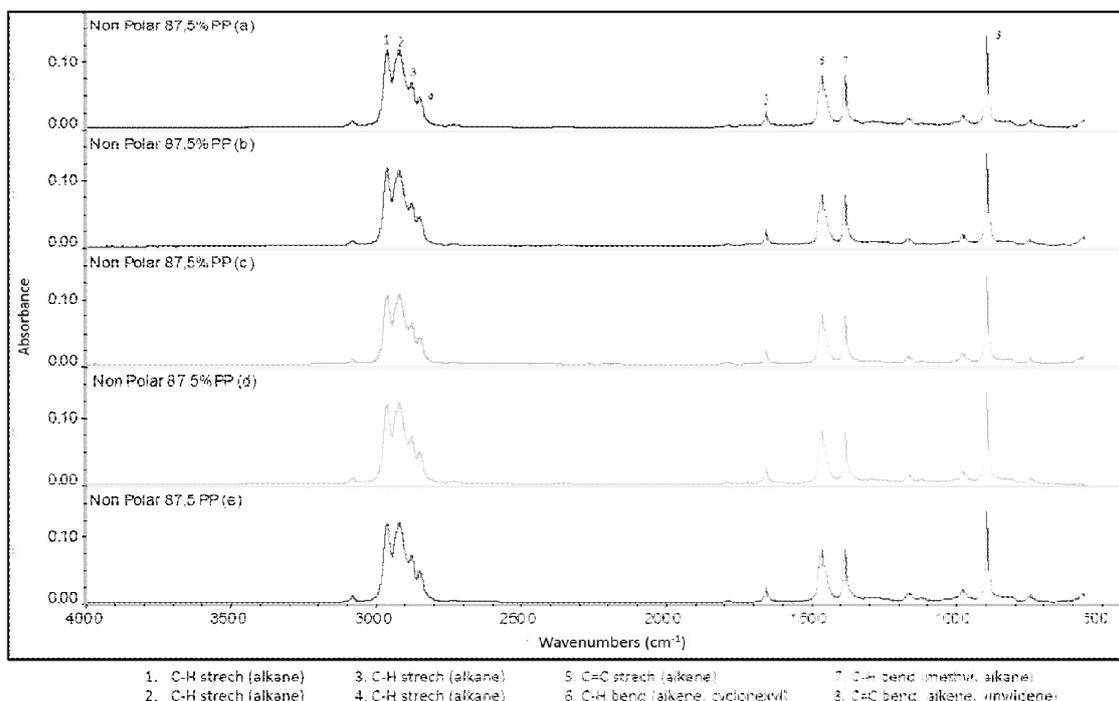


Fig. 2. FT-IR spectra of bio-oil from the first-stage pyrolysis

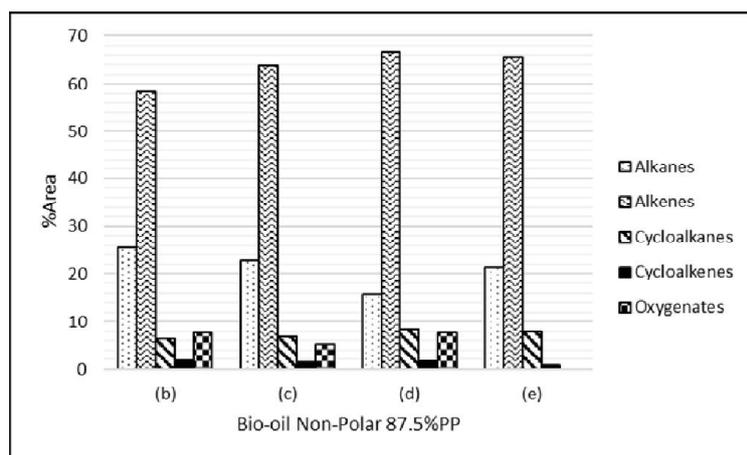


Fig. 3. Aliphatic composition of bio-oil produced by the first-stage pyrolysis

3.3. Second-Stage Pyrolysis Bio-oil Characterization

The kinematic viscosity of the bio-oil obtained from the second-stage pyrolysis was tested at 40°C and the measured viscosities of bio-oil obtained from the second-stage pyrolysis respectively are shown in Fig. 5. Viscosity of commercial gasoline and diesel measured for comparison are respectively 0.7 cStokes and 2.7 cStokes [9]. The viscosities of bio-oil resulting from the second-stage pyrolysis with the final temperatures of 200°C and 300°C were closer to the viscosity of gasoline. Viscosity of bio-oil from pyrolysis with the final temperature of 375°C was in between the viscosities of gasoline and diesel, while that from pyrolysis with the final temperature of 450°C was closer to the viscosity of diesel.

The bio-oil sampled from the second-stage pyrolysis were also characterized using GC-MS, LC-MS and H-NMR. Because of the low yield of bio-oil obtained from the pyrolysis with the final temperature of 200°C, this bio-oil was characterized using GC-MS and LC-MS only.

Fig. 6 shows that the compounds detected by GCMS mostly were of alkenes. The bio-oil characterization by H-NMR is shown in Table 1. H-NMR result shows that bio-oil resulting from pyrolysis with the final temperature of 300°C, 375°C and 450°C contained protons bonded to C=C chains respectively amounting to 7.03, 6.97, and 6.43%, which means that alkenes had much less composition than alkanes. The result of H-NMR differs from that of GC-MS because H-NMR can detect proton at alkanes with high molecular weights or long carbon chains which cannot be detected by GC-MS [13,14]. The reduction of alkene composition in bio-oil resulting from pyrolysis with higher final temperature means that higher temperature of the pyrolysis was unable to make more cracking on aliphatic chains, which is not expected. It seems there were condensation or polymerization reactions between double-bond carbon chains in competition with the cracking reactions [15]. It is suspected that the rate of polymerization reaction at higher temperature was higher than the rate of cracking reactions leading to net reduction of alkenes produced as suggested by Fig. 5 where higher final temperature in the second-stage pyrolysis produced bio-oil with higher viscosity.

Table 1. H-NMR analysis of bio-oil and gasoline

Hydrogen Types	Chemical Shift	% Amount of Protons in Bio-oil from First-Stage Pyrolysis	% Amount of Protons in Bio-oil from Second-Stage Pyrolysis Temperature of (%)			% Amount of Protons in Gasoline
			300°C	375°C	450°C	
Aromatics	7.2-6.0	0	0	0.01	0	8.83
Proton at C=C	6.0-4.5	6.03	7.03	6.97	6.43	0.74
Proton at OCH ₃ group bonded to guaiacyl, syringyl and lignin linkage	4.5-3.3	0	0.03	0.01	0.02	0
Proton at α-C bonded to C=C	3.3-1.8	17.82	23.24	22.38	20.52	18.14
Methyne (CH)	1.8-1.4	8.70	5.46	5.81	7.42	4.40
Methylene (CH ₂)	1.4-1.1	15.11	16.50	15.94	15.71	24.75
Methyl (CH ₃)	1.1-0.4	52.35	47.75	48.88	49.90	43.14

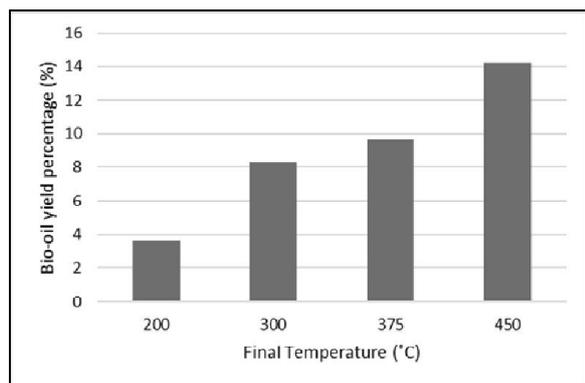


Fig. 4 Bio-oil yields in the second-stage pyrolysis at different final temperatures.

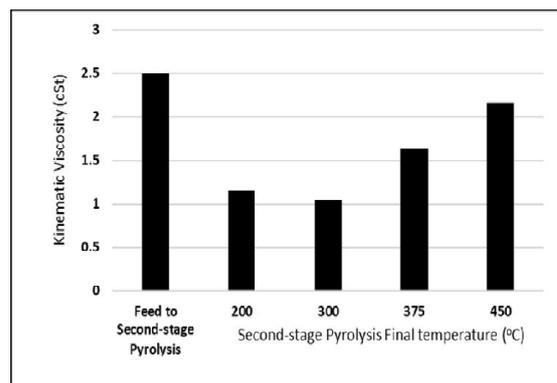


Fig. 5 Kinematic viscosity of bio-oil from the second-stage pyrolysis

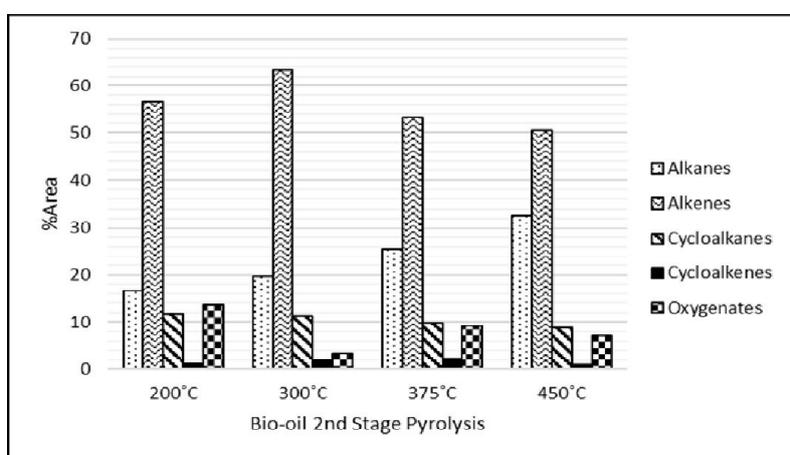


Fig. 6. Aliphatic composition of bio-oil from the second-stage pyrolysis

Comparing H-NMR analysis of the first-stage and the second-stage pyrolysis (see Table 2), combined proton composition attributed to methyl, methylene and methane, which represented alkanes in bio-oil, from the second-stage was lower than that from the first-stage pyrolysis, and consequently the composition of protons attributed to alkenes was higher. It suggests that in the second pyrolysis broken carbon chains resulted in more

double bond carbon chains under condition of lack of external hydrogen radical donation.

Oxygenate compounds associated to proton in the H-NMR result was very low (below 0.05%). This might have happened as long carbon chains, which had small polarity, were soluble in non-polar fraction when the separation of polar and non-polar fractions occurred.

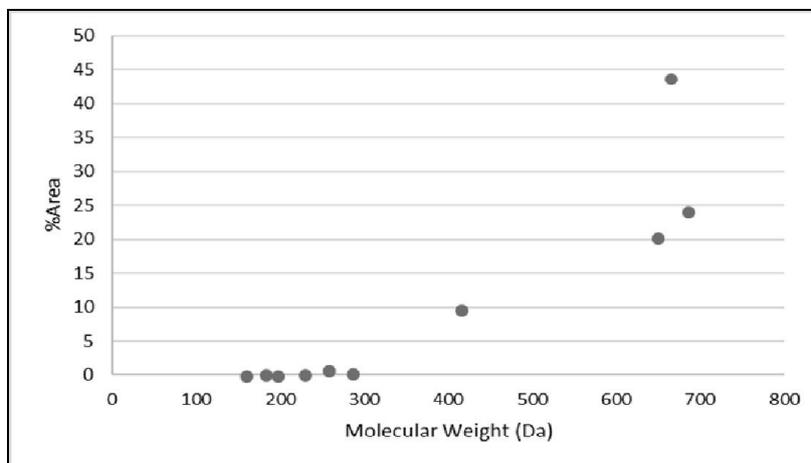


Fig. 7. Molecular weight distribution of bio-oil from first-stage pyrolysis

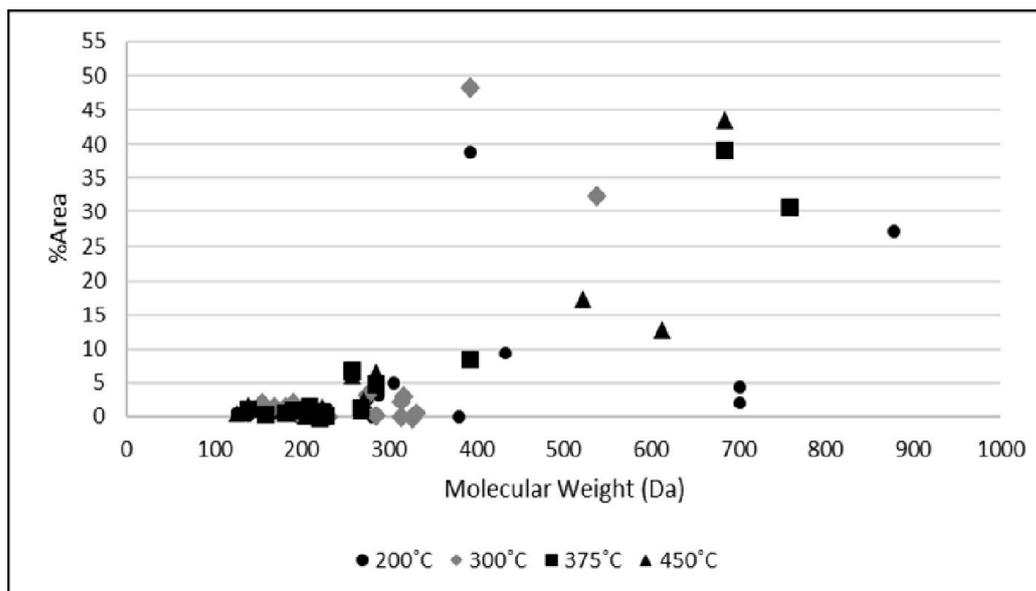


Fig. 8. Molecular weight distribution of bio-oil from second-stage pyrolysis

3.4. Molecular Weight Distribution of Bio-oil

Molecular weight distribution of bio-oil obtained by the first-stage pyrolysis is shown in Fig. 7, while for second-stage pyrolysis is shown in Fig. 8. The distribution data were obtained from LC-MS measurement, which can analyze the whole contents of bio-oil because LC-MS was capable of detecting high molecular weight compounds. Fig. 7 shows that the first-stage pyrolysis %area was dominated by molecular weight around 663 Da, 684 Da and 647 Da, with %area respectively 43.79%, 24.22% and 20.45%. Fig. 8 shows that at low molecular weights, all the second-stage pyrolysis bio-oil samples exhibit very low % area. However, as the molecular weight more than 400 Da, those samples demonstrated some differences. For example, bio-oil obtained from pyrolysis with final temperature of 200°C, %area was dominated by molecular weight around 391 Da and 876 Da, with %area respectively 39.07% and 27.45%. The bio-oil product from pyrolysis with final pyrolysis temperature of 300°C was dominated by molecular weight around 391 Da and 536 Da, with %area respectively 48.52% and 32.47%. It means that the average molecular weight of bio-oil from pyrolysis at 300°C was smaller than that at 200°C. This may have resulted that the earlier bio-oil had slightly lower viscosity than the latter bio-oil (see Fig. 5).

As the pyrolysis was carried out with final temperature of 375°C, the predominant molecular weights were around 758 Da with %area of 30.77%, 683 Da with %area of 39.19% and 395 Da with %area of 8.3%. For the bio-oil obtained by pyrolysis with final temperature of 450°C, the predominant molecular weights were around 520 Da with %area of 16.53%, 611 Da with %area of 13% and 683 Da with %area of

43.76%. These data of molecular weights show that the molecular weight distribution of bio-oil with final temperature of 375°C was more spreading than that of 450°C. The more concentrated molecular weight distribution of bio-oil with final temperature of 450°C seems to give higher viscosity than that of bio-oil with final temperature of 375°C. As far as the branching index is concerned, the earlier bio-oil had lower index than that of the latter bio-oil (see Table 2). Consequently, combined methylene and methyne groups in the earlier bio-oil were distributed in less number of carbon chains and gave in average longer branching. According to Khare et al [16] found that long branching attenuates the oil viscosity. Confronting the results above of the effect of molecular weight distribution and branching index on bio-oil viscosity, it suggests that the molecular weight distribution exerts more influence on the bio-oil viscosity.

Comparing the molecular weights of bio-oil obtained from the second-stage pyrolysis with final temperatures of 300 and 375°C exhibited in Fig. 8 shows the earlier had lower maximum molecular weight than the latter with significant difference. This may have resulted in viscosity difference, where the earlier was smaller than the latter.

3.5. Bio-oil and Gasoline Characteristics Comparison

To see whether the bio-oil has achieved similar characteristics to gasoline, the viscosity, BI, and HHV of bio-oil was compared to gasoline. The comparison is shown in Table 2.

Table 2. Comparison between bio-oil and gasoline

Requirements	First-stage Bio-oil	Second-stage Bio-oil			Gasoline
		300°C	375°C	450°C	
Kinematic Viscosity (cSt)	2.5	1.05	1.63	2.16	0.7
Branching Index	1.47	1.45	1.50	1.44	0.99
Higher Heating Value, HHV (MJ/kg)	47.36	47.46	47.45	47.40	54.57

Gasoline has branching index as well as kinematic viscosity lower than indices and viscosities attributed to bio-oil obtained from the second-stage pyrolysis. Considering the finding by Khare et al [16] that long branches, corresponding to low branching index, attenuates kinematic viscosity, it suggests that it is not molecular weight distribution inducing low viscosity of gasoline, but branching index. Therefore, effort of synthesizing bio-oil with characteristics approaching to those of gasoline should be directed to diminishing the branching index.

Table 2 shows that HHV values of all bio-oil samples had similar values and their values are close to gasoline's HHV value. For comparison, HHV value of bio-oil obtained from biomass pyrolysis has value around 18-26 MJ/kg because of containing a lot oxygenate compounds [14]. Based on the H-NMR data (see Table 1), the experimental bio-oil had low oxygenate compounds and consequently high HHV value.

4 Conclusion

From the analyzed data, it can be concluded that in order to obtain high yield of bio-oil, the second-stage pyrolysis be carried out under heating until a final temperature beyond the highest temperature of mass decomposition according to TGA data of bio-oil feed (375°C). However, the pyrolysis produced bio-oil with viscosity even larger than that of gasoline. The second-stage pyrolysis with final temperature of 300°C was the optimum temperature for obtaining bio-oil similar to gasoline because it has the lowest kinematic viscosity despite of highest alkenes composition according to H-NMR and low yield of bio-oil. It is recommended to do second-stage pyrolysis simultaneously with hydrogenation of the separated non-polar bio-oil to attain biofuel similar to gasoline.

Comparison of data of viscosities and branching indices of bio-oil obtained from the second-stage pyrolysis and gasoline suggests that in order to lower the bio-oil viscosity, the pyrolysis may be performed in coinciding with attempt of reducing branching index.

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