Feasibility study on the utilization of mahogany (*Swietenia macrophylla* King) wood as a raw material in the bio-oil production

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Abstract. The liquid fuels from biomass produced through fast pyrolysis is very promising due to their high energy density and carbon neutral properties. Therefore, the pyrolysis of Indonesian mahogany wood at various temperatures (450-600°C) was carried out in this study. A fixed-bed reactor was used in the pyrolysis experiments. The produced bio-oil, bio-char, and gaseous product were recovered and quantified. This study showed that the higher the temperature, the higher the yield of the bio-oil (39.40 wt% at 550°C). However, the pyrolysis at a temperature higher than 550°C produced a lower yield of bio-oil, possibly due to severe cracking resulting in more gaseous products. The produced bio-oils showed good characteristics, i.e. density of c.a. 1.17 g/mL, viscosity of 3.93-5.67 poise, total acid number of 0.66-0.79 mg-KOH/g, and calorific value of 16-18 MJ/kg. The water and volatile (acetic acid, furfural, phenol, and stearic acid) contents of the produced bio-oils were also quantified by using a gas chromatograph. The bio-oils with a low water content (13.46-15.90 wt%) and volatiles (0.1-2.9 wt%) were obtained, indicating high energy density and production of heavy molecules, respectively. The high acid number was likely from the heavy acids that could not be detected by the gas chromatograph.

1. Introduction

The energy demand of liquid fuels continues to increase, while the depletion of fossil-based energy resource continuously occurs. The liquid fuels were still the main favorable energy in Indonesia in the last 8-years period (2010-2018); 25% of the total 3.7 billion Oil Equivalent Barrels (SBM) [1]. A decrease in Indonesia's petroleum reserves of c.a. 37% has been observed in a 1995-2018 period [1]. This condition suggested that Indonesia's petroleum reserves was predicted to be exhausted in the next 11 years [1]. Therefore, an exploration of new and renewable energy resource is extremely important.

Biomass is considered as one of the most promising energy resources due its abundance and renewable properties [2]. A thermal conversion of lignocellulosic biomass through a pyrolysis technique would result in liquid fuels (is referred to as bio-oil) [2, 3]. Pyrolysis has been considered as the most promising and beneficial technique in the bio-oil production [3]. It involves the breakdown of the macromolecular components in the biomass into smaller molecules in the absence (or in the presence of limited amount) of oxygen [4]. Commonly, fast pyrolysis is used in the bio-oil production due to its high yield of the produced bio-oil. It requires a fast heating rate at high temperatures (300-650°C) with a short residence time of the vapor (1-2 seconds) [5].

In this study, Mahogany sawdust with a high content of lignocellulose was used. This type of wood is abundantly available in Indonesia. It showed a relatively high content of cellulose, hemicellulose and
lignin (approximately 47.26%, 27.37% and 25.82%, respectively) as was reported elsewhere [6], causing a feasible utilization as a starting material in the production of a high-yield bio-oil. In addition, the utilization of Mahogany wood sawdust was only about 20%, mainly as a mushroom planting media and waiting fuel [7], while the remaining 80% was still untapped. Therefore, utilization of Mahogany sawdust could be a very promising in the bio-oil production through fast pyrolysis and will be explained thoroughly in this paper.

Bio-oil is a viscous and blackish-brown mixture with acidic properties. Bio-oil contains many types of compounds ranging from very light compounds such as water and acetic acid to heavy ones such as sugar and lignin oligomers [8]. Bio-oil also contains 15-30% of water that could be derived from the thermal breakdown of hemicellulose, cellulose and lignin in the biomass [5,9]. The produced bio-oil can be further processed resulting in liquid fuels (bio-fuels), directly used as a fuel for boilers or be used as a substitute fuel for fossil fuels [9]. The feasibility of mahogany wood as a starting material in the bio-oil production through fast pyrolysis has been studied in this paper by investigating the effect of pyrolysis temperatures on the yields of the produced bio-oil. Further investigation on the characteristics of the mahogany wood-based bio-oils including their density, viscosity, heating value, water and volatiles contents and acid number was also carried out. It has been shown that the pyrolysis temperature showed a great influence on the yields as well as the characteristics of the bio-oil [10].

2. Methods
The production of bio-oil in this study was carried out through a fast pyrolysis technique of mahogany wood obtained from a wood industry in Central Java. Some standard chemicals were used in GC and GC-MS analyses in the quantification of water and volatiles in the bio-oil such as acetic acid (Merck, ≥99.85%), furfural (Merck, 99%), stearic acid (Merck, ≥98.5%), phenol (Merck, ≥99.5%), and demineralized water.

A fixed-bed type pyrolyzer equipped with thermocouples, a thermo-controller, and two condensers was used in the pyrolysis process of mahogany wood. Mahogany wood with a particle size of ≤400 μm was used. The pyrolysis was done at temperatures of 450-600°C with a controlled residence time of vapor of 1-2 seconds. The pyrolysis products (bio-oil, bio-char and gaseous products) were recovered and the yields were quantified to close the mass balance. In the case of the gaseous products, the yields were determined by difference.

The physical properties of the produced bio-oils i.e. density, viscosity, and HHV were determined by means of a pycnometer, Oswald viscometer, and bomb-calorimeter, respectively. The total acid number of the bio-oils was determined through a titrimetric method using potassium hydroxide solution and phenolphthalein as an indicator. The qualitative analysis of the volatiles in the bio-oils as well as the existence of water was carried out by means of a Shimadzu gas chromatograph equipped with a mass detector and an NIST library. The volatiles and water in the bio-oils was quantified by using an Agilent 6890 gas chromatograph equipped with an FID detector. Sets of standard solutions were used in the quantitative analyses of those substances.

3. Results and Discussion

3.1. Yields of pyrolysis products at various temperatures
The yields of pyrolysis products varied as the pyrolysis temperatures increased, as is shown in Fig. 1. Bio-oil was the targeted product in this study. An increase in the yield of the bio-oils by increasing the pyrolysis temperatures from 450°C to 550°C was observed. It was possibly due to the adequate cracking resulting in light-but-condensable molecules at those temperatures [11]. It could be also observed from the decrease in the yields of the bio-char by increasing temperature. However, the higher temperature (600°C) did not produce a higher yield of bio-oil; a slight increase in the yield of bio-oil was observed, possibly due to a severe cracking resulting in very light yet incondensible compounds [11]. It was evidenced by the increase in the yields of gaseous (incondensible) products, as can be seen in Fig. 1.
3.2. The characteristics of the bio-oils from the pyrolysis of mahogany wood

Mahogany wood was pyrolyzed resulting in bio-oil, bio-char, and gaseous products using a fixed-bed type pyrolyzer. The physical appearance of the bio-oil and bio-char produced from the pyrolysis of mahogany wood in this study was presented in Fig. 2. The produced bio-oil was a dark-brown and viscous liquid with a smoky-typical smell. In addition, the bio-char produced was carbonaceous solid material with black color.

![Figure 2. The physical appearance of (a) bio-oil and (b) bio-char produced from pyrolysis of mahogany wood at 550°C.](image)

To study the feasibility of mahogany wood as a raw material, the physical and chemical properties of the bio-oils produced in this study were investigated. The properties included density, viscosity, calorific value, water and volatiles contents were shown in Table 1 and Table 2. The density and viscosity of the bio-oil produced from the pyrolysis of mahogany wood in this study decreased by increasing pyrolysis temperatures. It was in line with the increase in the yield of bio-oil produced by increasing temperature, as is shown in Fig. 1. More cracking of macromolecules in the biomass apparently occurred by increasing temperatures resulting in lighter condensable molecules in the bio-oils. The higher content of the light molecules in the bio-oils would lead to a lower density and viscosity of the corresponding bio-oils [12]. These lower density and viscosity of the bio-oils observed in this study were likely also due to the higher water content of the bio-oils. However, the water content of the bio-oils produced in this study was much lower indicating the high energy density that can be proven from their calorific value, as is shown in Table 1.
The content of GC-detectable light compounds was investigated in this study and is shown in Table 2. These light compounds greatly affect the reactivity and stability of the bio-oils produced [19]. It would also provide a great influence on the behavior of the bio-oils in the further processing, e.g. hydro treatment resulting in bio-fuels and/or fine chemicals [20, 21]. The content of volatiles in the bio-oils produced in this study was quite low. It indicated that the production of heavy molecules during the pyrolysis of mahogany wood was more pronounced than that of light ones. Moreover, the bio-oils from mahogany wood showed a high total acid number. These acids were probably from the cracking of side chains of hemicellulose and cellulose as the constituent of the biomass feedstock. The low content of light acids (e.g. acetic acid) shown in Table 2 indicated that the quantified acids was likely from the acids with high molecular weight and GC-undetectable molecules. This would need a great effort to overcome the high acidity of the bio-oils. Although the bio-oils from the pyrolysis of mahogany wood produced in this study most likely contained a high content of heavy molecules, the low content of water and the good physical properties such as density, viscosity, as well as calorific value indicated the great potential of mahogany wood as a starting material in the bio-oil (liquid fuel) production through fast pyrolysis technique.

### Table 1. Physical and chemical properties of the bio-oils produced from the pyrolysis of mahogany wood at temperatures of 450-600°C.

| Properties                        | Pyrolysis temperature (°C) | References | Commercial diesel |
|-----------------------------------|----------------------------|------------|-------------------|
|                                   | 450 | 500 | 550 | 600 | [13-17] | [18] |
| Density (g/mL)                    | 1.17 | 1.17 | 1.16 | 1.15 | 0.94-1.20 | 0.815-0.860 |
| Viscosity (Poise)                 | 5.67 | 5.08 | 4.33 | 3.93 | 2.5-5.5 | 2.0-4.5 |
| Calorific value (MJ/kg)           | 16.20 | 17.17 | 17.84 | 18.12 | 15.0-20.0 | 35.97 |
| Total acid number (mg-KOH/g-BO)   | 0.68 | 0.66 | 0.73 | 0.79 | 0.8 | 0.6 |
| Water content (wt%)               | 13.46 | 14.80 | 15.90 | 15.67 | 15-30 | 0.05 |

The content of GC-detectable light compounds was investigated in this study and is shown in Table 2. These light compounds greatly affect the reactivity and stability of the bio-oils produced [19]. It would also provide a great influence on the behavior of the bio-oils in the further processing, e.g. hydro treatment resulting in bio-fuels and/or fine chemicals [20, 21]. The content of volatiles in the bio-oils produced in this study was quite low. It indicated that the production of heavy molecules during the pyrolysis of mahogany wood was more pronounced than that of light ones. Moreover, the bio-oils from mahogany wood showed a high total acid number. These acids were probably from the cracking of side chains of hemicellulose and cellulose as the constituent of the biomass feedstock. The low content of light acids (e.g. acetic acid) shown in Table 2 indicated that the quantified acids was likely from the acids with high molecular weight and GC-undetectable molecules. This would need a great effort to overcome the high acidity of the bio-oils. Although the bio-oils from the pyrolysis of mahogany wood produced in this study most likely contained a high content of heavy molecules, the low content of water and the good physical properties such as density, viscosity, as well as calorific value indicated the great potential of mahogany wood as a starting material in the bio-oil (liquid fuel) production through fast pyrolysis technique.

### Table 2. The content of volatiles in the bio-oils produced from pyrolysis of mahogany wood at temperatures of 450-600°C compared to other types of biomass.

| Content of volatiles (wt%) | Pyrolysis temperature (°C) | Bagasse [15] | Rice straw [22] | Bamboo | Africana birch [23] |
|----------------------------|-----------------------------|--------------|-----------------|--------|--|------------------|
| Acetic acid                | 2.89 | 3.00 | 3.05 | 2.85 | 59.72 | 5.73 | 4.53 | - |
| Phenol                     | 1.13 | 1.18 | 1.31 | 1.38 | 5.07 | 2.70 | 0.82 | - |
| Furfural                   | 0.49 | 0.54 | 0.56 | 0.56 | 3.00 | 9.29 | - | - |
| Stearic acid               | 0.10 | 0.10 | 0.11 | 0.11 | - | - | 5.00 | |

4. Conclusions

The bio-oils produced from the pyrolysis of mahogany wood showed good physical properties including viscosity (3.93-5.67 Poise), density (1.15-1.17 g/mL), and calorific value (16.20-18.12 MJ/kg). The low water content (13.46-15.90 wt%) of the bio-oils indicating a high energy density was another good characteristic of the produced bio-oils, despite of its high content of heavy molecules indicated by the low volatile content in the bio-oils. The high acid content (indicated by the total acid number of 0.68-0.79 mg-KOH/g bio-oils) with the low volatile content would be a tough challenge in the production of bio-fuels through e.g. hydrotreatment and/or hydrodeoxygenation. Efforts to reduce the acidity of the bio-oils through e.g. esterification and solvent addition, would be highly important and would be reported in the upcoming paper.
5. Acknowledgments
The authors would like to thank Universitas Negeri Semarang for the financial support through a Research Grant of University Research Excellence. The authors also would like to thank Ms. Yuan Maylia Rosanti for the GC and GC-MS analyses on the bio-oil samples.

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