Characterization of Slow Pyrolysis Products of *Macaranga motleyana*: Effect of Sample Size

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**Abstract.** The characterization of biocrude oil produced by slow pyrolysis of fast growing wood *Macaranga motleyana* has been conducted. Slow pyrolysis was carried out in a fixed bed pyrolysis reactor at 500 °C for 1 hour with a variety of wood sample size. The decrease of a sample size from 20 to 40 mesh resulted in an increase in the percent yields of liquid product, which were 28.5 wt.% and 36.1 wt.% respectively. Characterization of the biocrude oil showed that the pH of the biocrude oil was 2, the density of biocrude oil was 1.132 g/mL, while the viscosity value of the biocrude oil was 53.6 cSt. Analyses of the biocrude oil using a Gas Chromatography-Mass Spectrometry (GC-MS) revealed that the biocrude oil derived from *Macaranga motleyana* wood contained phenol and its derivatives, such as eugenol and compounds resulted from thermal degradation of cellulose or hemicellulose. The use of sample with a smaller sample size resulted in biocrude oil containing more chemical compounds.

1. Introduction

Exploration and exploitation of fossil fuels on a large scale in recent decades is not balanced with the formation process in a short time. This prompted some researchers to look for alternative energy substitutes for fossil fuel energy sources. One alternative source of substitute for fossil energy can come from the bark, logs, grass or other plants. *Macaranga* spp wood is one of the endemic plants of East Kalimantan that has the potential as an alternative energy source. *Macaranga* is a pioneer plant that grows in tropical forests which are classified as fast-growing plants and are easily found in large numbers [1]. *Macaranga motleyana* contains lignin, cellulose and hemicellulose which are potential to be fuel energy sources [2].

One method for converting lignocellulosic material into an energy source is pyrolysis. Pyrolysis is a thermochemical conversion process at temperatures from 650 to 800 K and at low pressures that occur in the absence of air and reducing gases to convert material (e.g biomass) to liquid (bio-oil), solids (charcoal), and gas [3-5]. Biocrude oil or liquid smoke is a blackish-colored liquid resulting from the pyrolysis of biomass such as wood, bark and other biomass [6-10]. Pyrolysis yield is affected by temperature, time and particle size. It was found that particle size can affect the value of the activation energy of mixed wood sawdust pyrolysis, the yield of phenolic compounds and linear hydrocarbons, and the production of CO and CO₂ gases [11]. In the slow pyrolysis process, biomass is heated at low heating rates and long vapor residence time [12]. This method produces not only liquid products but
also char that can be used for several applications. Previously, slow pyrolysis of *Macaranga gigantea* produced a quite substantial amount of liquid products [6]. Thus, slow pyrolysis of the other species of *Macaranga* (e.g. *Macaranga motleyana*) is worth studying. *Macaranga motleyana* (and also other species) is also worth exploiting because this plant is considered a weed. The use of *Macaranga motleyana* as a fuel producing material will increase the added value of this plant. In this report, the physical and chemical characteristics of slow pyrolysis products of *Macaranga motleyana* with several sample sizes are analyzed and studied.

2. Materials and methods

2.1. Sample preparations
*Macaranga motleyana* samples were obtained from the Education Forest of Mulawarman University in Taman Hutan Raya Bukit Soeharto, Loa Janan, Kutai Kartanegara, Indonesia. The bark of the wood sample was peeled. The wood sample was then chopped and dried in the sun for ±7 days until the water content in the sample was reduced. After that, the sample was mashed using a hammer mill to 20 and 40 mesh.

2.2. Sample analysis
The ash content and moisture content of *Macaranga motleyana* were calculated using the ASTM methods. The wood lignin content (Klasen lignin) was determined by TAPPI T 222 om-88 method [13] and determination of α–cellulose content were performed using TAPPI T 9 m-54 method [14].

2.3. Pyrolysis experiments
Slow pyrolysis of *Macaranga motleyana* wood was carried out using a laboratory-scale batch reactor as described in previous studies [6]. About 250 g of wood samples (20 and 40 mesh size) were charged into the sample container in the pyrolysis reactor. Slow pyrolysis runs were conducted at 500 °C for 1 hour. The time needed to reach the pyrolysis temperature from room temperature was about 15 minutes. The resulting liquid product consisted of two phases. The top layer was the aqueous phase and the blackish-brown bottom phase was the organic phase (bio-oil). The two phases were separated by a separating funnel and then weighed. The yields of organic phase, aqueous phase, and solid residue were calculated as described in Sinaga et al. [6]. Characterization of the organic phase was performed using a Gas Chromatography-Mass Spectrometry (GCMS QP 2010S SHIMADZU). The acidity (pH), viscosity, and density of the organic phase were determined.

3. Results and discussions
Ash content, moisture content, lignin, cellulose and hemicellulose contents of *Macaranga motleyana* are shown in Table 1. Cellulose and hemicellulose contents in *Macaranga motleyana* samples are considerably high, so the wood species has the potential to produce large quantities of pyrolysis products because cellulose and hemicellulose can produce volatile compounds that are easy to condense [7]. The content of lignin in *Macaranga motleyana* wood can determine the temperature and time of pyrolysis because lignin has a very complex structure. Wood with a high lignin content will tend to produce aromatic compounds (e.g. phenol and its derivatives) and charcoal [8].

| Wood species          | Moisture content (%) | Ash content (%) | Hemicellulose (%) | α-cellulose (%) | Lignin (%) |
|-----------------------|----------------------|-----------------|-------------------|----------------|------------|
| *Macaranga motleyana* | 11.05±0.06           | 0.76±0.04       | 3.4 ± 1.6         | 68.8 ± 1.6     | 37.6 ± 1.1 |

Table 1. Moisture content, ash content and chemical content of *Macaranga motleyana*. 
Table 2. Yields (%) of organic phase (bio-crude oil), aqueous phase, and char from slow pyrolysis of Macaranga motleyana.

| Sample size | Organic phase (%) | Aqueous phase (%) | Char (%) |
|-------------|-------------------|-------------------|----------|
| 20 mesh     | 2.5±0.2           | 26.2±0.7          | 13.3±0.7 |
| 40 mesh     | 5.4±0.5           | 30.7±1.2          | 11.6±0.7 |

| Liquid yield (%) | Char (%) |
|------------------|----------|
| 18 mesh*         | 20.88    | 30.00    |
| 60 mesh*         | 3.25     | 22.63    |

*Slow pyrolysis of Imperata Cylindrica at 500 °C [15]

Table 3. List of identified compounds in the chromatograms of the organic phase obtained from slow pyrolysis of Macaranga motleyana.

| No. | Compounds                        | RT (min) | %area | No. | Compounds                        | RT (min) | %area |
|-----|----------------------------------|----------|-------|-----|----------------------------------|----------|-------|
| 1   | Phenol                           | 12.0     | 6.7   | 1   | Butyrolactone                    | 9.2      | 9.3   |
| 2   | 3-methyl-1,2-cyclopentanediode   | 13.6     | 1.4   | 2   | Phenol                           | 12.0     | 5.1   |
| 3   | 2-methyl phenol                  | 14.7     | 3.6   | 3   | 2-methyl phenol                  | 14.7     | 2.3   |
| 4   | Mequinol                         | 15.7     | 8.9   | 4   | Mequinol                         | 15.7     | 4.2   |
| 5   | 2,6-dimethyl phenol              | 16.5     | 1.1   | 5   | 2,6-dimethyl phenol              | 16.5     | 2.3   |
| 6   | 2,3-dimethyl phenol              | 17.9     | 8.1   | 6   | 2,3-dimethyl phenol              | 17.9     | 3.2   |
| 7   | 2-methoxy-4-methyl phenol        | 19.2     | 8.5   | 7   | 2-methoxy-4-methyl phenol        | 19.2     | 5.8   |
| 8   | 4-ethyl-2-methoxy phenol         | 21.8     | 6.6   | 8   | 2-ethyl-4-methyl phenol          | 20.9     | 1.5   |
| 9   | 4-(1-methyl propyl) phenol       | 24.1     | 3.9   | 9   | 4-ethyl-2-methoxy phenol         | 21.8     | 4.4   |
| 10  | 2-methoxy-4-propyl phenol        | 24.4     | 3.2   | 10  | 2,6-dimethoxy phenol             | 24.0     | 3.1   |
| 11  | Hexadecanoic acid                | 24.5     | 2.2   | 11  | Hexadecanoic acid                | 24.5     | 8.5   |
| 12  | Eugenol                          | 25.6     | 1.4   | 12  | Eugenol                          | 25.6     | 4.1   |
| 13  | 4-hidroxy-3-methoxy benzoic acid | 26.7     | 5.5   | 13  | 4-hidroxy-3-methoxy benzoic acid | 26.7     | 2.2   |
| 14  | Dodecane                         | 27.9     | 1.8   | 14  | 1,2,3-trimethoxy-5-methyl benzene| 28.7     | 1.5   |
| 15  | 1,2,3-trimethoxy-5-methyl benzene| 28.7     | 1.7   | 15  | Dodecane                         | 29.8     | 2.3   |
| 16  | Dodecanoic acid                  | 29.8     | 1.9   | 16  | Isopropyl myristate              | 35.7     | 4.7   |
| 17  | 2-heptadecanone                  | 37.4     | 1.2   | 17  | 2-heptadecanone                  | 37.4     | 1.7   |
| 18  | Methyl ester hexadecanoic acid   | 37.9     | 3.5   | 18  | Methyl ester hexadecanoic acid   | 37.9     | 5.4   |
| 19  | 9-octadecanoic acid              | 41.4     | 1.9   | 19  | 9-octadecanoic acid              | 41.4     | 3.8   |
| 20  | Methyl ester-9-octadecanoic acid | 41.5     | 1.1   | 20  | Methyl ester-11-octadecanoic acid| 41.5     | 2.2   |

* lignin derived compound, **cellulose/hemicellulose derived compound

Pyrolysis of Macaranga motleyana produced gas, liquid products and char. Wood pyrolysis with a particle size of 40 mesh produced higher yields of organic phase and aqueous phase and a smaller char yield than that with a particle size of 20 mesh (Table 2). This is presumably due to pyrolysis of wood with smaller particle size (40 mesh) (thus, greater surface area) will cause a faster heat transfer process,
so that the thermal decomposition of lignin, cellulose and hemicellulose is more optimal. It was found that if lower particle size feedstock is used, slow pyrolysis may lead to the increase in gas production (lower yields of liquid and solid) due to cracking of heavy molecules (tar) [15](Table 2). Thus, it is important to note that the selection of sample size must consider the desired pyrolysis product. The organic phase (biocrude oil) produced has dark, aromatic, smoke-like characteristics. Biocrude oil produced has a pH of 2, a density of 1.132 g / mL and a viscosity of 53.6 cSt. The high acidity of the organic phase was probably because of the presence of acetic acid and other acids resulting from thermal degradation of lignin, cellulose and hemicellulose (Table 3). The density value depends on the compounds in the sample, if the sample contains large molecular weight compounds, then the density value obtained is higher. The viscosity of *Macaranga motleyana* biocrude oil is different from the viscosity of biocrude oil from other biomass samples [2]. This is because the viscosity value is affected by the type of sample used, pyrolysis temperature, water content in oil and the pyrolysis reactor used [16].

Chromatograms of *Macaranga motleyana* wood biocrude oil are presented in Figure 1. In the chromatogram of 20 mesh biocrude oil there were 65 compounds observed, whereas in that of 40 mesh biocrude oil there were 82 compounds were observed. This shows that the sample size affects the composition of compounds produced in pyrolysis of the wood sample. The compounds with the highest 20 percent area identified in the *Macaranga motleyana* biocrude oil were shown in Table 3. These compounds were from decomposition and degradation of lignin, cellulose, and hemicellulose. The formation of products derived from hemicellulose and cellulose, e.g. hexadecanoic acid, ketones, occurred at around 200-260 °C and 240-350 °C [2]. Phenol and its derivatives and aromatic hydrocarbons were thermal degradation products of lignin, which occurred around 400 °C[17].
Figure 1. Chromatograms of the organic phase obtained from slow pyrolysis of *Macaranga motleyana* (a. 20 mesh; b. 40 mesh)

4. Conclusions

The wood particle size affected the yields of the liquid products and the solid residue and also the chemical composition of the liquid products. Pyrolysis of 40 mesh *Macaranga* wood produced higher pyrolysis yields and biocrude oil containing more chemical components than that of 20 mesh sample. The compounds in *Macaranga motleyana* wood biocrude oil were the result of thermal degradation and decomposition of cellulose, hemicellulose and lignin.

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