Slow pyrolysis of fast growing wood *Macaranga gigantea*

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**Abstract.** Slow pyrolysis of fast growing wood *Macaranga gigantea* has been studied. The product yields and chemical composition of products obtained from the experiments under different conditions (temperature, reaction time, sample mass) were described. In all cases, *Macaranga gigantea* gave total product yields, ranging from 45-65%. The increase in temperature and reaction time resulted in the increase in product yields. The organic phase of the pyrolysis products contained phenol and its derivatives, furans, benzene and its derivatives, eugenol and the isomers, methyl esters, aromatic ketones, poly-aromatic hydrocarbons, and carboxylic acids; these compounds were mainly derived from lignin, cellulose and hemicellulose.

1. **Introduction**

At present, the most frequently used energy source comes from fossils (gas and petroleum), but its utilization is considered to give a rise in the level of greenhouse gases. Renewable energy sources such as biomass are potential to be developed to reduce the CO$_2$ emission in the atmosphere resulted from the use of fossil fuels. Alternative fuels, such as biofuels, can also overcome the limited availability of fossil based fuels in the future.

Biocrude oil could be obtained from thermochemical conversion processes from biomass such as gasification, pyrolysis and liquefaction [1,2]. During pyrolysis, the thermal decomposition process occurs without the presence of oxygen [3]. For lignocellulosic biomass, the main constituents such as hemicellulose, cellulose and lignin can be converted into liquid fuel and utilized as an energy source through the pyrolysis process [4].

*Macaranga* is known as the first species classified as fast growing species in tropical forest ecosystems. However, the utilization of Macaranga for fuel purposes is very limited [5]. The lack of basic information regarding its function and suitability as raw materials for fuel and energy production is believed to be the main reason and factors that hinder the utilization of this wood species. Macaranga wood has substantial amount of lignin and cellulose to be used as a source of energy [6]. Thus, Macaranga is very potential to be used as a raw material in the production of biocrude oil. This paper reports pyrolysis yields and product composition of biocrude oil produced from slow pyrolysis of one species of *Macaranga* (*Macaranga gigantea*) under different reaction conditions.
2. Materials and Methods

2.1 Sampel Preparations
The samples used in this research were *Macaranga gigantea* woods which were previously taken from the Education Forest of Mulawarman University in Taman Hutan Raya Bukit Soeharto, Loa Janan, Kutai Kartanegara. The wood samples were chipped and dried in air until water content was reduced and were then used as raw material in the pyrolysis process. A small portion of the wood samples were crushed to powder (100 mesh) for use in the analysis of chemical content.

2.2 Sample Analysis
The moisture content and ash content of the wood samples were determined. The lignin content, hemicellulose and α-cellulose content were analysed by Klason lignin procedure (TAPPI T 222 om-88), TAPPI T 9 m-54 and TAPPI T 9 m-54, respectively.

2.3 Pyrolysis Process
Pyrolysis runs were carried out in a laboratory scale batch reactor. Approximately 150-250 g sample was loaded into the sample chamber and then the chamber was assembled with the pyrolysis reactor circuit. Pyrolysis runs were carried out at 300-400 °C and the reaction time (15-45 minutes) was started after the desired temperature was reached (initial temperature of the sample chamber was 35 °C and heating up time was ±30 mins). The liquid product consisted of organic phase and aqueous phase were collected and weighed as well as the char in the sample chamber. The total yield, the yield of organic phase (biocrude oil) and aqueous phase were calculated as follow:

\[
\text{Yield of organic phase (biocrude oil)} \% = \frac{\text{weight of organic phase (g)}}{\text{sample initial weight (g)}} \times 100\% \quad (1)
\]

\[
\text{Yield of aqueous phase} \% = \frac{\text{weight of aqueous phase (g)}}{\text{sample initial weight (g)}} \times 100\% \quad (2)
\]

\[
\text{Total yield} \% = 100\% - (\text{yield of char}) \quad (3)
\]

\[
\text{Yield of char} \% = \frac{\text{weight of char (g)}}{\text{sample initial weight (g)}} \times 100\% \quad (4)
\]

2.4 Biocrude oil Analysis
The organic phase (biocrude oil) was analysed by Gas Chromatography-Mass Spectrometry (GCMS-QP2010S SHIMADZU) to identify the chemical compound in the product. The pH, density and viscosity of the biocrude oil were also determined.

3. Result and Discussion

3.1 Analysis of wood sample
The moisture content, ash content and chemical content of *Macaranga gigantea* were presented in Table 1. The high content of cellulose and hemicellulose in the wood sample makes it possible to produce a high yield of liquid product because cellulose and hemicellulose are the main sources of volatile compounds that are easily condensed [7]. Whereas if the wood contains substantial amount of lignin, a higher pyrolysis temperature and a longer reaction time will be required to decompose the lignin due to the very complex lignin structure. High lignin content will also produce more aromatic compounds and char [8].
### Table 1. Moisture content, ash content and chemical content of *Macaranga gigantea*

| Species          | Moisture Content (%w/w) | Ash Content (%w/w) | Hemicellulose (%) | α-cellulose (%) | Lignin (%) |
|------------------|-------------------------|--------------------|-------------------|-----------------|------------|
| *Macaranga gigantea* | 10.68                   | 0.68               | 5.41 ± 0.7        | 66.48           | 31.01 ± 1.0 |

3.2 *Total pyrolysis product*

The total product yield from pyrolysis of *Macaranga gigantea* under different reaction conditions can be seen in Figure 1. Based on the figure, it can be concluded that reaction temperature and reaction time affect the total pyrolysis product. The increase in pyrolysis temperature and reaction time resulted in the increase in the total yield from around 45% to 65% and the decrease in char production. The higher temperature that being used, then the thermal decomposition of chemical component of Macaranga wood such as lignin, cellulose and hemicellulose became greater [9]. At 350 °C the conversion of samples to products was higher than that at 300 °C because at this temperature the hemicellulose and cellulose in the wood were almost completely decomposed [10]. While at 400 °C, more than 60% of the wood samples were converted to pyrolysis products because most of the lignin content in wood began to decompose at 400 °C [9]. The total yield of pyrolysis did not depend on the total pyrolysis yield.

![Figure 1](image-url)  
*Figure 1. Total pyrolysis yield of *Macaranga gigantea* with different (a) reaction temperature, (b) reaction time, (c) sample mass*
3.3 Liquid product yield

Liquid products obtained from the pyrolysis process consisted of 2 different phases. The upper phase was an aqueous phase in the form of orange smoky smelling liquid mainly consisting of water and partly decomposition of the polar chemical component in wood samples. The other phase was the organic phase (biocrude oil) in the form of viscous black liquid which was decomposition products of lignin, cellulose and hemicellulose in the wood. The increase of pyrolysis temperature and reaction time affected the production of liquid product (Figure 2). After the vapor condensation, liquid product can be collected up to 70 wt% on a dry weight basis [10,11].

![Image of liquid product yield](image)

**Figure 2.** Liquid product yield from pyrolysis of *Macaranga gigantea* with different (a) reaction temperature, (b) reaction time, (c) sample mass

3.4 Characterization of biocrude oil

The pH and physical characteristics of the organic phase (biocrude oil) obtained from pyrolysis of *Macaranga gigantea* was presented in Table 2. The pH of biocrude oil obtained was 2. According to Bridgewater [3], the pH of biocrude oil derived from wood is usually around 2.5 and the acidity of biocrude oil is caused by the chemical content of biocrude oil, which is mostly dominated by phenol derivatives and carboxylic acids (See Table 3). The density of biocrude oil was around 1.1 cSt. The density of biocrude oil was similar to biooil produced in other studies [3].
Table 2. pH and physical properties of biocrude oil from pyrolysis of *Macaranga* wood

| Wood species         | pH   | Density (g/mL) | Viscosity (cSt) |
|----------------------|------|----------------|-----------------|
| *Macaranga gigantea* | 2    | 1.102          | 19.40           |

The chromatogram of biocrude oil produced from pyrolysis of *Macaranga gigantea* was presented in Figure 3. Around 30-40% of the composition of biocrude oil was dominated by phenol derivatives such as phenol, methyl phenol, dimethyl phenol, trimethyl phenol, ethyl phenol, propyl phenol, methoxy phenol, dimethoxy phenol and hydroxy methoxy phenol (Table 3). These compounds are obtained from the degradation of lignin that occurs during the pyrolysis process. Eugenol (7-9%), isoeugenol (1.4-1.8%) and vanillin were identified in the chromatograms which were also compounds produced by lignin degradation [13]. Thermal degradation products of cellulose and hemicellulose (e.g. acetic acid) were also observed in the chromatograms of the biocrude oil.

![Chromatogram of biocrude oil produced from pyrolysis of *Macaranga gigantea*](image)

Figure 3. Chromatogram of biocrude oil produced from pyrolysis of *Macaranga gigantea* (reaction temperature = 400 °C, reaction time =30 minute, sample mass = 250 gram)

Table 3. Major compounds observed in the chromatogram of biocrude oil produced from pyrolysis of *Macaranga gigantea* (reaction temperature = 400 °C, reaction time =30 minute, sample mass = 250 gram)

| Retention time (min) | Compound                               | % area |
|----------------------|----------------------------------------|--------|
| 2.18                 | Acetone                                | 3.5    |
| 8.39                 | 2-furancarboxaldehyde                  | 2.6    |
| 17.06                | 2-methyl-phenol                        | 4.7    |
| 18.24                | 4-methoxy-phenol                       | 10.1   |
| 21.66                | 2-methoxy-4-methyl-phenol              | 11.7   |
| 24.30                | 2,3-dimethoxytoluene                   | 11.4   |
| 26.48                | 2,6-dimethoxy-phenol                   | 4.2    |
| 29.13                | 1,2,4-trimethoxy-benzene               | 3.0    |
| 29.30                | Eugenol                                | 8.1    |
| 31.10                | 1,2,3-trimethoxy-5-methyl-benzene      | 3.3    |
| 35.50                | 2,6-dimethoxy-4-(2-propenyl)-phenol    | 2.8    |
4. Conclusion
The pyrolysis yield of *Macaranga gigantea* depended on reaction temperature and reaction time. The sample mass generally did not have any effect on product yields. The organic phase of the pyrolysis product was acidic due to the presence of substantial amount of phenolic compounds. The chemical compounds observed in the biocrude oil were pyrolysis or thermal degradation products of the major constituent of *Macaranga gigantea*, lignin, cellulose and hemicellulose.

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