Effect of pyrolysis temperature on bio-fuel quality produced from pine bark (Pinus merkusii) by pyro-catalytic method

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Abstract. This study aims to determine the effect of pyro-catalytic temperature on the quality of bio-fuel. Bio-fuel quality analysis includes: density, viscosity, calorific value, and composition of hydrocarbon compounds using Gas Chromatography-Mass Spectrometry (GC-MS). The pyro-catalytic process was carried out at a temperature variation of 400, 500 and 600°C with each addition of 5% zeolite catalyst to the mass of the sample used. Results showed the best bio-fuels were obtained at a temperature of 500°C with viscosity of 21.39 cP, density of 0.9884 g/ml and calorific value of 10.367 kcal/kg. Analysis composition of fuel content in bio-fuel using GC-MS obtained acetic acid, phenol, furfural, pyridine, cresol, benzene, ethanol and catechol with a fuel percentage of 66.51% at 500°C, so as to produce bio-fuel from Pine bark (Pinus merkusii) can be used as an energy source (alternative fuel).

1. Introduction
Bio-fuel is the main product of biomass rapid pyrolysis which has many applications in the energy and fuel fields [1,2]. Development of bio-fuel can replace the position of hydrocarbon fuels in the industry, such as for combustion engines, boilers, static diesel engines, and gas turbines. Bio-fuel is very effective as a substitute for diesel, heavy fuel oil, light fuel oil, and for various boilers [3].

One of the potential biomass for use in making bio-fuel is pine bark (Pinus merkusii) [4,5]. The content of holocellulose and lignin pine bark is 59.38% and 40.43%, higher the content of holocellulose, rate of product formation will be better. Materials containing cellulose have the potential to be used as raw material for bio-fuels [6].

Bio-fuel is a black-colored liquid fuel derived from biomass such as wood, bark and other biomass industrial wastes. Pyrolysis is one of them significant technology that can utilize various types of lignocellulosic biomass to produce different bioenergy fuels, like bio-oil, pyrolytic gas and bio-char [7,8,9]. However, the presence of oxygenated compounds, such as phenol and alcohol in bio-oils makes it very acidic and unstable for the suitable transportation fuel. These oxygenated compounds can be converted into hydrocarbons which can be cured using different methods homogeneous or heterogeneous catalyst [10,11].

Zeolites and metal-zeolites have been widely applied for catalytic biomass pyrolysis that have shown promising deoxygenating activity for bio-oil because they are highly acidic in nature and exhibit competitive shape-selectivity properties due to micro/meso pore sizes [12]. Zeolite-based catalysts usually deoxygenate the biomass components via dehydration, decarboxylation and decarboxylation
reactions [13]. These catalysts not only decrease the quantity of oxygenated compounds in the bio-oil but also increase the amount of hydrocarbons (aliphatic and aromatic), therefore, upgrading the carbon content in bio-oil and making it more efficient to use as a transportation fuel.

In the research, conversion of pine bark waste into bio-fuel is carried out by the pyro-catalytic method with zeolite catalyst, where the pyro-catalytic process is carried out at temperatures of 400, 500 and 600°C. Bio-fuel quality test is carried out with several analyzes, namely, density, viscosity, calorific value and hydrocarbon content with GC-MS instruments. Several researchers have conducted an analysis of the content of compounds in bio-fuel using GC-MS instruments [5,14]. This research will study the effect of temperature on the production and quality of bio-fuel produced from the pyro-catalytic process of pine bark waste (*Pinus mercussi*).

2. Materials and Methods

2.1. Materials and instrumental
The material used in this study was a sample of pine bark waste (*Pinus mercussi*) taken from pine forests in the Muna island region, Southeast Sulawesi. Instrument used is a series of pyrolysis devices, Gas Chromatography-Mass Spectrometry (GC-MS), filter paper (*whatman*), pycnometer, viscometer, and container.

2.2. Sample preparation
Pine bark waste (*Pinus mercussi*) is first washed to remove the remaining dirt, then the water content is removed by drying in the sun and chopped with a size of 5-8 cm.

2.3 Bio-fuel production by the pyro-catalytic method
Pyro-catalytic process of pine bark waste (*Pinus mercussi*) was carried out at temperatures of 400, 500 and 600°C using a zeolite catalyst at a ratio of 5%. In all experiments, 500 g of raw material was put into the pyrolysis reactor. Then the pine bark is put into the reactor and heated for each temperature variation.

2.4 Bio-fuel characterization

2.4.1 Density Analysis
Density of fuel-oil was analyzed using a 25 ml picometer, then calculated and measured according to ISO 4787 standards [15,16].

2.4.2 Viscosity analysis
Viscosity is determined by comparing viscosity bio-fuel and viscosity of comparative liquid in the form of water using an ostwald [15].

2.4.3 Calorific value analysis
Calorific value is analyzed by involving variable density, specific gravity and API (American Petroleum Institute) gravity. Specific gravity is the ratio between the density of fuel-oil with the density of water, while the value of API gravity is calculated using the following equation [15,17].

\[
{^\circ API} = 141.5 \div SG - 131.5
\]  

\[
CV = \frac {2.2046226} {3.9673727} \times (18.650 + 40 \times (^\circ API - 10)) \text{ kcal/kg.} \quad [17]
\]

2.4.4 Gas chromatography-mass spectrometry (GC-MS) analysis
The chemical identification of bio-fuel hydrocarbons was carried out by the GC-MS instrument using a DB-5 column (60 m x 0.25 mm x 0.25 µm) agilent, injector temperature was 280°C, and the carrier gas
separation ratio was 69.4 the carrier gas was helium in the flow control of 1 mL/min. Initially, the oven temperature is kept at 45°C for 2 minutes, then the temperature rises to 280 °C at 5 °C / minute and held for 2 minutes [14].

3. Results and Discussion

3.1. Bio-oil physical characterization

The physical characteristics of rendemen, water content, density, viscosity, and calorific values. Pyro-catalytic process involves decomposition of organic compounds that make up the structure of materials forming hydrocarbons [18]. Based on the research, it is found that influence of temperature on physical characteristics of bio-fuel pine bark as shown in the following table.

| Temperature (°C) | Rendemen (%) | Water content (%) | Density (gr/ml) | Viskosity (cP) | Calorific value (kкал/ kg) |
|------------------|--------------|------------------|----------------|--------------|--------------------------|
| 400              | 36.2         | 2.4              | 0.9967         | 22.635       | 10,341                   |
| 500              | 33.8         | 1.2              | 0.9884         | 21.392       | 10,367                   |
| 600              | 32.0         | 2.0              | 0.9981         | 21.201       | 10,336                   |

Increase in pyrolysis temperature causes the percentage of yield of bio-fuel to decrease. High temperatures will increase rate of cracking where breaking chains of compounds in the material will occur more quickly so that the water content and volatile compounds will evaporate quickly. However, when the reaction temperature is raised beyond its optimum temperature there is a decrease in the expected percentage of liquid product conversion. This is because during the cracking process, fractions of lighter hydrocarbons are produced more so that many gases cannot be completely condensed [19].

In this study the water content was analyzed using the deanstark method. Water content in bio-fuel greatly affects quality of the fuel. Water content of the bio-fuel is expected to be as low as possible in order to produce a high calorific value and will produce bio-fuel that is easy to ignite or ignite initially. Water content and calorific value are inversely proportional [20].

Based on Table 1, density obtained from pine bark bio-fuel is in the range of 0.9884-1.0066 gr / ml. This is consistent with the range of conventional bio-fuel values, namely 0.94-1.2 gr/ml [21]. Low density values indicate good bio-fuel quality [22]. The amount of density at temperatures 400°C and 600°C is influenced by the molecular weight of the components contained in the bio-fuel. The higher the molecular weight, the greater the density produced [23].

Table 1 shows the connexion of pyrolysis temperature with viscosity of bio-fuel which is inversely proportional to the increase in temperature causing the value of viscosity will be smaller. This is due to higher temperature of the bonding bond in molecule [24]. The lower the viscosity value of a fuel, the easier it will be to flow. Viscosity produced in this study is included in the range of values from conventional bio-fuel which is 10-150 cP and lower than diesel oil which is 35-50 cP [3].

Calorific value is an important parameter needed for a fuel to show the energy content in the fuel [25]. The calorific value of bio-fuel depends on several factors, such as water content, oxygen content and the operating conditions of the pyrolysis process. High levels of water contained in bio-fuel can absorb heat during the combustion process, causing evaporation. This evaporation process causes the calorific value of bio-fuel to decrease and causes calorific value to be low. Meanwhile, if the oxygen content and water content in bio-fuel are few, it will produce a higher calorific value [26]. The calorific value in most bio-fuels was found to always have a lower calorific value than conventional petroleum fuels, namely 9553.83-11,942.29 kcal/kg [27]. This proves that the calorific value of pine bark bio-fuel is included in the conventional petroleum range so that it can be used as an alternative fuel source.
3.2 Analysis gas chromatography-mass spectrometry (GC-MS)
Identification using the GC-MS method was carried out to determine the distribution of compound components at variations in temperature of bio-fuel from pyrolysis of pine bark. The results of breaking spectra on GC-MS on pyrolysis bio-fuel are shown in Figure 1.

![Figure 1. GC-MS analysis results of pine bark bio-fuel at temperatures (a) 400°C (b) 500°C (c) 600°C.](image)

Based on GC-MS analysis data, the peaks in chromatography are components in bio-fuel which are mostly the result of cellulose, hemicellulose and lignin decomposition. The content of compound that dominates at 400°C is acetic acid with an area of 10.85% percent. Acid compounds in bio-fuel are able to kill bacteria so that it affects the shelf life of bio-fuel products [28]. The compound that dominates at 500 °C is Furfural with a percent area of 16.08%. The furan content increases as effect of the first secondary reaction of cellulose products. The content of the compound that dominates at 600 ° C is Catechol with 13.66% percent area. Catechol is a colorless and water soluble compound. Catechol is commonly used for pepticides, gasoline and alizarin synthesis (C14H8O4). The content of the compound obtained is a component of the compound needed to be used as an alternative fuel.

The bio-fuel produced is identified as having fuel component compounds. The identification of the pine-bark bio-fuel compound can be seen in Table 2.
Aained at a temperature of 500°C can be produced as an alternative fuel source as substitute for diesel fuel and conventional fuel. The differences in the components of pyrolysis compounds at each temperature are caused by differences in the composition of hemicellulose, cellulose and lignin. However, from this temperature variation, the largest fuel constituent was obtained at a temperature of 500°C with a percentage of 66.51%.

4. Conclusions
Based on the results of analysis that has been done shows that the optimum pyrolysis temperature to produce the best bio-fuel is obtained at a temperature of 500°C with a fuel content of 66.51% and a calorific value of 10,367 kcal / kg. Thus pine bark waste (Pinus merkusii) can be produced as an alternative fuel source as substitute for diesel fuel and conventional fuel.

Table 2. Identification of pine bark bio-fuel fuel compounds.

| Compound Name | Formula | Area (%) | 400°C | 500°C | 600°C |
|---------------|---------|----------|-------|-------|-------|
| Acetic acid   | CH₃COOH | 10.85    | 1.69  | 11.01 |
| Phenol        | C₆H₅OH | 16.52    | 35.83 | 10.85 |
| Furfural      | C₅H₄O₂ | 6.22     | 20.23 | 7.91  |
| Pyridine      | C₅H₅N  | 2.81     | 1.57  | 2.03  |

Table 3. Identification of pine bark bio-fuel fuel compounds (continued).

| Compound Name | Formula | Area (%) | 400°C | 500°C | 600°C |
|---------------|---------|----------|-------|-------|-------|
| Creosol      | C₆H₆O₂ | 3.25     | 5.48  | 2.79  |
| Benzene      | C₆H₆   | 13.95    | 0     | 19.57 |
| Ethanol      | C₂H₅OH | 1.73     | 1.71  | 1.10  |
| Jumlah Total |         | 55.33    | 66.51 | 55.26 |

Based on the data in Table 2, it is known that the main organic components contained in biofuels are those containing acids, esters, alcohols, ketones, aldehydes, akenes, furans and other aromatic compounds which are constituent characteristics of the fuel. These characteristics make biofuels an environmentally friendly fuel. The differences in the components of pyrolysis compounds at each temperature are caused by differences in the composition of hemicellulose, cellulose and lignin. However, from this temperature variation, the largest fuel constituent was obtained at a temperature of 500°C with a percentage of 66.51%.

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