Influence of temperature pyrolysis and biomass size particles on characterization of bio oil derived from Pinus Merkusii flower

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Abstract. Increased human populations induce enhanced developments in industry, transportation, infrastructure and other areas. To date, the energy needed to supply these areas is still mainly derived from fossil fuels. Renewable fuels become an attractive alternative for replacing fossil fuels that are being on the skids. Bio oil is one of the alternative energy sources resulting from biomass pyrolysis process. The purpose of this study is to obtain the bio oil characteristics of Pinus Merkusii flower in vary of temperatures and sizes of biomass powder, those were temperatures of 450 – 550°C and sizes of 0.644 mm and 0.456 mm. Dry pine flower powder was inserted into a fixed bed reactor enclosed by furnace. Prior heating, the N2 gas was flown through the reactor to dissipate the O2 gas present in the reactor. After the N2 gas stream was stopped, the reactor was run in isolated condition. Pyrolysis run at heating rate of 15 °C/min and residence time for 3 hours. From the existing variations, the largest bio oil yield i.e. 45.2011% was obtained from the sample size of 0.644 mm at temperature of 550°C. The resulting bio-oil had the following properties: dark brown, pH of 2.682 – 4.053; density of 1.01 - 1.145 gr.cm³; viscosity of 58.544-103.465 mm².s⁻¹; acetic acid content of 21 – 49.2 mg.cm⁻³ and the heating value of 10.850 - 11.663 MJ.kg⁻¹. The bio oil was potential to be biofuel and bio-chemical materials through upgrading process.

Keywords: Pinus Merkusii flower, bio-oil, pyrolysis, characterization

1. Introduction
Currently, the energy crisis is being a big concern. The main source of energy today is still derived from petroleum processing. The growth of human population and industries causes increasing energy demand. However, petroleum reserves are continuously reduced. One of the ways which can overcome the problem is using alternative energy from biomass. Indonesia is the largest biomass energy developer in Southeast Asia. Biomass potential in Indonesia reaches 32,654 MW, while the installed capacity is 1,171 MW [1]. Compared to other renewable energy, biomass energy conversion process...
is cheaper. Biomass such as from corncobs, wood, bark, bagasse, or other biomass containing lignocellulose can be processed into alternative energy by pyrolysis [2,3,4].

In the pyrolysis process, biomass is heated under oxygen-free conditions to produce bio-char, bio-oil and non-condensable gas, where the results highly depend on operating conditions. Some important parameters in the pyrolysis process are heating rate, pyrolysis temperature, and residence time in the reaction zone. Generally, the heating rate conducted is between 5 - 100°C/min [5]. Further, the pyrolysis is usually carried out in the medium temperature range of 350 - 600 °C compared to the gasification process that uses a high temperature range of 800-1000 °C [5,6]. During the pyrolysis process, the very large and complex hydrocarbon molecules of biomass will break into relatively small and simple molecules in the form of gases, liquids and solids.

Energy produced from biomass by pyrolysis process is in the form of bio oil, gas and bio-char. Bio-oil consists of carbon, hydrogen and oxygen with very little sulphur content. The largest organic components in bio-oils are lignin, alcohol, organic acids, and carbonyls. These characteristics make bio-oil as an environmentally friendly fuel [6]. Bio-oil is dark-coloured liquid which smells like smoke and comprises a very complex mixture of oxygenated hydrocarbons with some proportion of water coming from original moisture and reaction product [7]. Further, the nature of pyrochemical biomass, reaction condition, and the technology used in thermal decomposition predispose bio oil composition [8]. Bio oil produced from biomass pyrolysis mainly contains aromatics, aliphatic, naphthenic hydrocarbons and oxygenated compounds [5]. Due to those compounds, bio oil has the potential to become a fuel source such as fossil fuels for energy supply. Therefore, biomass residues and leftovers for biofuels propose an alternative option to substitute fossil fuels with no additional land use. Additionally, bio oil can be refined into high value chemicals [5,7]. The requirement for fast pyrolysis bio oil used as biofuel is expressed in ASTM D 7544-12 [9]. There are two grades of bio oil which reflect their quality namely Grade G and Grade D. Grade G is referred to use only in industrial burners, whereas Grade D is for use in commercial/industrial burners requiring lower solids and ash content. However, residential heaters, small commercial boilers, engines, or marine applications could not utilize these grades. The requirements for grade G and D on some properties are the same, i.e. HHV of 15 MJ/kg.min., kinematic viscosity at 40°C of 125 mm²/s⁻¹ max. and density at 20°C of 1.1 - 1.3 kg.dm⁻³ [9].

One of biomass as a source of bio oil is pine flower. *Pinus Merkusii* is the only type of pine native to Indonesia. Wood waste and pine bark have been widely used in previous studies as a source of bio oil [10,11]. However, the utilization of pine flowers to date mostly used as handicraft materials. Based on a review by Almendros et al. [12], the pine flowers from Granada were potentially used as fuel-producing biomass. Pine flowers have a high volatile material content based on its proximate analysis.

In this research, the pyrolysis experiment of the *Pinus Merkusii* flowers was accomplished in fixed-bed reactor to investigate optimum condition of pyrolysis process and characteristics of bio oil. Some properties of bio oil produced were analysed using complementary analytical techniques to evaluate the bio oil potential as fuel or chemical feedstock.

2. Materials and Methods

2.1. Materials and samples preparation

The biomass used is pine flowers obtained from pine forest Mangunan Bantul Yogyakarta Indonesia. Solar drying step was applied to the pine flowers before being ground. Then the pine flower was screened to obtain particle size of 0.644 and 0.456 mm. Prior to use in pyrolysis process, biomass samples were dried in an oven for 30 minutes at 105°C to reduce water content. Proximate test was then applied to a small of dried biomass. The proximate test results are shown in Table 2.

2.2. Experimental procedure

The pyrolysis process was carried out in an isolated fixed-bed reactor located within the furnace. A 500 gram biomass sample was purged into the reactor, and then N₂ gas was fed into the reactor for 15 minutes to dissipate the O₂ gas present in the reactor. An electric furnace was used to heat the reactor.
The temperature was monitored using Ni-Cr-Ni thermocouple placed inside the reactor. The experiment was undertaken using two variables; those were temperature and size particles of biomass. It was conducted at the temperature of 450, 500 and 550°C for two particle sizes. Once the biomass was put in and the \( \text{N}_2 \) gas was flown for 15 minutes, the reactor was heated with a heating rate of 15°C/min. After reaching the desired temperature, condition was maintained for isothermal reaction for 3 hours.

![Figure 1. Set of pyrolysis devices](image)

Gas pyrolysis products were passed through a series of condensers which used ice water as a cooling medium. The total liquids obtained from condensing were then pondered to ascertain the yield. The bio-char collected from the reactor was also weighted. Further, the non-condensable gas was determined based on the difference between the raw materials and the result of bio-oil and bio-char yields [13].

2.3. Characterization

Proximate analysis of the pine flower was conducted based on the ASTM D-3172-13. Calorific values of biomass and bio-oil were procured as higher heating value (HHV) with Gallenkamp Auto Adiabatic Bomb Calorimeter according to ASTM D 240. Additionally, other properties specified from the experimental bio oil results were density (ASTM D854), viscosity (ASTM D445), pH (ASTM E70-07), and acetate acid content (ASTM D 1613-17).

3. Results and discussion

3.1. Proximate analysis

The ash content varies greatly depending on the type of biomass which can vary from very low content (0.1%) in the rubber seed shell [14] to very high one (around 34.6%) in rice husk [15]. Table 1 showed that the ash content of pine flower was moderate. The high ash content of biomass could be a challenge in the furnace due to higher probability of ash deposition and slags like incrustations, as well as corrosion of the surfaces of the furnace [16]. Besides, it may lead to char formation since inorganic compounds in ash could catalyse the formation of char during pyrolysis [13]. On the other hand, the ash content could inhibit enzymatic hydrolysis of biomass such as in saccharification of biomass samples [14]. The higher ash content could hamper the process.

The moisture content of biomass considerably varies from very low content such as in hornbeam shell (2.28%) [5] to high one in the rubber seed shell (14.3%) [14]. As shown on Table 2, the moisture content of pine flower in this study was quite low. The moisture content is a notable operation parameter, but it often fluctuates [13]. Varying moisture contents may complicate furnace operations and cause uncertainty of energy content in the fuel delivered to the plant. Furthermore, the moisture
content is able to govern the combustion processes leading to negatively affect the calorific value. It also disrupts transportation costs, drying, storage and handling of the biomass [16].

Table 1. Proximate analysis result of Pinus Merkusi flower

| Pine flower | Analysis results |
|-------------|-----------------|
|             | Ash content, (% wt) | Moisture content, (% wt) | Volatile matter, (% wt) | Fixed Carbon, (% wt) | Calorific value, (MJ/kg) |
| Pine flower | 3.018 | 3.377 | 63.677 | 29.928 | 20.639 |

The determination of volatile matter and fixed carbon contents are notable, since it can exhibit the potential of these materials to produce energy through combustion. High amount of volatile matter indicates that the material can generate a high gaseous pyrolysis products and it is also able to facilitate the ignition process of the solid with the temperature [12]. The volatile matter content of the biomass sample of the study was average, but it was still lower than Granada’s pine cone [12]. Meanwhile, the fixed carbon content was quite high compared with hornebeam shell, Colombia’s bagasse, Granada’s pine cone, and rubber seed shell and kernel [5,8,12,14]. The fixed carbon was often related with the char formation [16]. It is the leftover remained after devolatilization process [12].

Calorific value (CV) is defined as the amount of energy conceived in a fuel. The Pinus Merkusi flowers contented 20.693 MJ/kg calories and it was higher compared to some Brazil’s biomass which has calorific value between 12.5 until 19.07 MJ/kg [16].

3.2. Pyrolysis product yields

Reaction temperatures were significantly influence the yields of various pyrolysis products. Figure 2 reflected that the optimum bio oil yield was obtain at temperature of 550 °C for particle size of 0.644 but it was at 450 °C for particle size of 0.456 mm. Some studies found out that the optimum pyrolysis temperatures to obtain optimum bio oil yield were between 500 – 550 °C [5,8,13,17] using different biomass. An interested occurrence was took place on Figure 2(a) where there was inconsistent bio oil yield with increasing temperature. At 450 °C as the beginning of the process, there was an optimum volatilisation process from biomass where the bio oil yield was 42.49%. Rising temperatures to 500°C caused the bio oil yield incisively dropped to 27.097% but gas yield enhanced significantly from 20.03% to 35.54%. This could be induced high secondary cracking reactions of pyrolysis vapours and volatilisation of the char which caused the high formation of gas and decreasing bio-oil yields. By elevating continually the temperature to 550°C, the contrast phenomenon ensued where the bio-oil product much increased to 45.20% while the gas product drops drastically to 21.22%. Therefore, the maximum bio oil yield was obtained at 550°C. This trend was in contrast to the study by Montoya [8] that temperature rise from 500-550°C led the bio oil yield fell. This could be possible due to depolymerisation and oligomerisation process of gases to form condensable gases which may be aided by the presence of a catalyst in the ash [13]. In addition, the volatilization process of char also continued occurring with enhancing temperatures leading to decreasing of the char.

Different phenomenon was viewed from Figure 2(b) for the smaller biomass size, where increasing temperature consistently declined bio oil yield from 39.51% to 25.31%. The highest bio oil yield was obtained at temperature of 450°C. This was reflected that the higher temperature caused dropping the bio oil yield, which was in accordance with the study by Montoya [8]. However, some studies exhibited that the bio oil yield increased with elevating temperature to 525 or 550°C, and then it dropped at temperature higher than 525 or 550°C [5,19]. The reaction occurred could be dehydration, depolymerisation, repolymerisation, defragmentation, and rearrangement [15]. Higher temperature provided more energy so that it broke hydrocarbon bonds leading to an increase in the devolatilise process. This was coupled with the smaller particle size which could help to incline the heating rate
However, this trend was distinct to the yields of char and gas. With rising temperatures to 500°C, the char yields enhanced quite sharply and conversely, the gas yields decreased steeply. This could be provoked by high depolymerisation and oligomerisation process of the gas leading to the char formation due to availability of catalyst activity of the ash [13]. Moreover, there could be aromatization process which upgraded small oxygenated compounds and light olefins such as ethylene and propylene in the pyrolysis vapour into aromatic compounds. This process led to eliminate water, carbon monoxide and carbon dioxide [18]. Furthermore, increasing the temperature to 550°C caused dropping of the char and sharp rising of the gas yield. This could be higher temperature leading to the promotion of secondary cracking reactions of pyrolysis vapors as well as the secondary decomposition of char due to the catalytic activity of the ashes [13].

![Figure 2](image1.png)

**Figure 2.** Yield of pyrolysis products at different pyrolysis temperatures (a) particle size 0.644 mm; (b) particles size 0.456 mm

![Figure 3](image2.png)

**Figure 3.** Yield of bio oil pyrolysis at different sizes of biomass particles

The change in particle size of this study gave a different trend as shown on Figure 3. The optimum bio oil yield for particle size of 0.644 mm was obtained at high pyrolysis temperature i.e. 550°C compared to the smaller one of 0.456 mm which had optimum pyrolysis temperature at 450°C. The volatilization process of the smaller particles could be faster than the larger one. This was related with the particle heating rate, where the bigger particles were heated slower compared the smaller one leading to less volatile material released [8]. It rendered the smaller particles reached the optimum bio oil yield faster i.e. at temperature of 450°C compared the bigger particles. Further, the faster heating rate due to temperature rose can cause secondary cracking reaction and result in decreasing bio oil produced. On the other hand, the bio oil product on the larger particle size was averagely higher than
the smaller one, except the product at temperature of 500°C. This was possibly because the slower heating rate on the large particles led to the primary and secondary cracking reaction run longer compared to the smaller particles. Therefore, the volatile material of this size was gained much more than the smaller one. While, the trend occurred at temperature of 500°C was in line with the trend ensured in the study conducted by Montoya [8]. Of the two variables studied, the optimum bio-oil was obtained from biomass particles size of 0.644 mm and pyrolysis temperature of 550°C.

3.3. Bio oil properties

The characteristics of bio oil were shown on Table 2. Averagely, densities obtained were in the range of 1.01 – 1.145 gr.cm\(^{-3}\) which were smaller compared to bio oil densities from other studies [5,17,20] and the density requirement for Grade G [9]. However, this value was still higher compared to densities of diesel and heavy fuel oil i.e. 0.827 and 0.980 kg.dm\(^{-3}\), respectively [5]. The fuel density is corresponded with the engine performer because the fuel injection volume becomes the elementary for the injection process on the machine. The kinematic viscosities of the study are between 58.544 and 103.465 mm\(^2\).s\(^{-1}\), where these values were still lower than the requirement for Grade G [9], but it was comparable with bio oil viscosity of rice husk [21]. High viscosity effects on the flow characteristic of oil and its atomisation characteristics [5].

Due to influential content of organic acids such as acetic acid and formic acid, the characteristic acid is always associated with bio oil through pH value and acid content. The pH values of most bio oils are between 2 and 3 [20]. The pH and acid content of the bio oil obtained was in the range of 2.682 to 4.053 and 21 to 49.2 mg acetic acid.cm\(^{-3}\), respectively. The pH value was in accordance with the pH of pyrolysis bio oil from residual chanar, palm fruit, and rice husk [17,21], but it was higher than bio oil’s pH from sugarcane bagasse with molasses [20]. In fact, the low pH value of bio oil correlates with acid content. The acidity, that causes corrosion especially at high temperature, becomes one of the reasons to establish bio oil conditioning process prior to be directly used as fuel [21]. Eventually, the heating values of the bio oil were between 10.580 and 11.663 MJ.kg\(^{-1}\) which were still lower compared to the requirement for Grade G [9]. According to field observations, the gas liquor obtained was mixture of aqueous phase, viscous tar and a little solid. Prior to performing physical properties, separation of solid particles with liquids was carried out. It led some viscous tar retained in the filter media. As a matter of fact, the tar contributes a high calorific value compared to the aqueous phase [22]. Besides, low calorific of the bio oil values are also influenced by the high degree of oxygenated compounds and water content [15]. Consequently, this induced falling of the bio oil calorific value.

Table 2. Characteristics of bio oil derived from pine flower *Pinus Merkusii*

| Temperatures, (°C) | Particle sizes (mm) | Parameters |
|------------------|-------------------|------------|
|                  | Density, (g.cm\(^{-3}\)) | Viscosity, (mm\(^2\).s\(^{-1}\)) | pH | Acetic Acid, (mg.cm\(^{-3}\)) | Calorific value, (MJ.kg\(^{-1}\)) |
| 450              | 0.644              | 1.02       | 95.294 | 2.925 | 30 | 10.580 |
|                  | 0.456              | 1.02       | 59.314 | 3.521 | 36.6 | 10.726 |
| 500              | 0.644              | 1.05       | 63.809 | 2.682 | 49.2 | 11.044 |
|                  | 0.456              | 1.01       | 103.465 | 2.931 | 33.6 | 11.144 |
| 550              | 0.644              | 1.03       | 58.544 | 3.91  | 21.6 | 11.367 |
|                  | 0.456              | 1.144      | 71.316 | 4.053 | 21  | 11.663 |
The characteristics of bio oil approached to Grade G requirements are indicated by bio-oil resulted from pyrolysis process with a particle size and a pyrolysis temperature of 0.644 mm and 550°C, respectively. The sample shows that its density and viscosity values are meet the permitted conditions. Besides, its heating value is still relatively higher than the other bio oil samples. To meet the grade G bio oil requirements which can be used as fuels for heating boilers and burners, the heating value is increased without separating the tar from condensed gas. Besides that, other physical properties such as flash points, ash, solid, water and sulphur content need to be analysed to complete the grade G bio oil specifications.

Pyrolysed bio oil from Pinus Merkusii flowers shows the potential as fossil fuels substitute for heating boilers and burners. By upgrading the pyrolysis process using catalysts, the high grade bio oil obtained can be used to supersede fossil fuels for internal combustion engines and the chemicals obtained can supply the chemical industry.

4. Conclusion
In this study, analysis was applied to the biomass and the bio oil pyrolysis results. The result of proximate analysis of Pinus Merkusii flower showed that volatile matter content of 63.677% and heating value of 20,639% indicated the potential of energy and chemicals from the biomass. The study was conducted to determine the effect of pyrolysis temperature between 450 -550°C and the particle size of biomass on pyrolysis process. The trend of pyrolysis results occurred on these two particle sizes was dissimilar. By enhancing temperature, the larger particle size i.e. 0.644 mm, exhibited an inconsistency of bio-oil yields which was associated with the gas yield. However, the biochar yield little dropped constantly. The optimum bio oil was obtained at 550°C. Whereas, the smaller biomass size, which was 0.456 mm, indicated that the bio-oil yields decreased steadily with rising temperatures and then, the highest bio oil yield was achieved at 450°C. Moreover, the gas yields were inconsistent inversely proportional to the char results. Different particle size depicted the distinction of optimum temperature to produce maximum bio oil due to different heating rate occurred on the process. In addition, the heating rate of pyrolysis process led the larger biomass particles tend to generate more bio oil. The resulting biofuels meet several requirements as a Grade G of biofuel. Through the upgrading process, the quality of biofuels will be more mounted. Accordingly, this will produce good prospecting chemicals.

Acknowledgment
The authors are grateful for the financial support from the Chemical Engineering Department, Faculty of Industrial Technology, University of Islamic Indonesia.

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