

Bio-Oil from Pyrolysis of Pine Fruit as Renewable Alternative Energy Using Ni/Mo/Zeolite as Catalyst

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ABSTRACT

Reserves for fossil fuels as energy sources are increasingly depleting, while the need for these fuels is increasingly higher along with the population growth. Regarding that solution needs to be sought one of them by utilizing the alternative energy. At the other hand the use of fossil fuels have a negative impact on the environment. This will require renewable substitute fuels, one of which is the utilization of bio-oil from the pyrolysis process of biomass such as pine fruit. This pyrolysis process produces bio-oil, biochar, and gas which can all be utilized, both bio-oil and biochar can be used as the alternative fuels. Bio-oil was formed through pyrolysis process with the pine fruit that mixed Ni/Mo/Zeolite catalyst. Pyrolysis was carried out in the fixed bed reactor at the temperature of 550, 600, and 650oC respectively with the time of pyrolysis of 1, 2, 3, and 4 hour respectively. The mass ratio of mass of catalyst to mass of pine fruit was 3 g/100 g, and inert condition in the reactor is served by flowing nitrogen as 80 mL/minute. In this case study, it was found that the highest yield of 19.96% was achieved at 600oC for 4 hours. At temperatures above 600oC it is found that the bio-oil yield decreased. The density of bio-oil was ranging from 0.83 to 0.94 gr/mL and the viscosity was ranging from 1.42 to 1.48 cSt. The heating value of bio-oil was ranging from 7,600 to 8,300 cal/gr. The bio-oil obtained has a standard that meets the quality as an alternative fuel. The other product was biochar which the heating value 6,400 to 6,760 cal/gr and can also use as solid fuel.

Key words : Alternative energy, Bio-oil, Biochar, Fossil fuels, Pyrolysis.

1. INTRODUCTION

The world's main energy source is fossil fuels whose use has increased from year to year. Fossil fuels have a negative impact on the environment because it produces gas emissions. Therefore, another renewable energy source is needed in the form of biomass. Biomass is an abundant, diverse and cheapest resource in the world. The use of biomass has

attracted worldwide attention in recent years because of its superiority to overcome the problem of environmental pollution and energy shortages. One of the renewable energy sources that can be developed is energy from pine fruit [1].

Pine fruit comes from pine tree (*Pinus merkusii*) which grow in Indonesia. Pine fruit can be pyrolysed to produce bio-oil and bio-oil is then used as an energy source [2], [3]. Bio-oil has the characteristics of a liquid with a dark color and smells like smoke. Bio-oil can be produced using various methods. Pyrolysis is a process of degradation of biomass by heat in the absence of oxygen to produce gas, bio-oil and biochar [4]. Pyrolysis is divided into three different types namely fast pyrolysis, intermediate pyrolysis, and slow pyrolysis. In fast pyrolysis (600oC) and short heating time (<10 minutes) the resulting product is predominantly liquid (bio-oil), intermediate pyrolysis (500oC) and heating time (10-15 minutes) the resulting product is in the form of bio-oil yield which is low, whereas pyrolysis is slow (400oC) and heating time (> 15 minutes) the resulting product is dominant in the form of solids (bio-char) [5]. The pyrolysis method is better for producing bio-oil in the form of liquid products, but when compared with the gasification or combustion method it only produces 5% and 30%, while the pyrolysis can achieve 75% results [6, 7]. The pyrolysis process of pine fruit powders using zeolite as catalyst can reach the bio-oil yield as high as 8.1% [8]. Pyrolysis process usually occurs at a temperature of 225oC-325oC and to obtain a good bio-oil yield needed the catalyst.

The catalyst usually use the metal's active side and generally the metal that is often used is a transition metal. In the chemical industry, the type of transition metal most widely used is nickel (Ni) and molybdenum (Mo) [9]. Nickel (Ni) is used as a hydrogenation catalyst and molybdenum (Mo) is used as a hydro cracking and desulfurization catalyst. Ni and Mo metals are generally used in a carrier to increase the effectiveness of the metal catalyst. Zeolite is a low-cost carrier material and is available in various sizes. Zeolite is the hydrated alumino-silicate chemical compound with the cations of sodium, potassium and barium. Zeolite has a large

pore distribution and surface area. Between Zeolite, Ni, and Mo metals will be combined and be modified to produce catalysts with different characteristics and much more effective [10]. In this pyrolysis process a Ni/Mo/Zeolite catalyst is used in order to increase the amount of bio-oil produced.

In the pyrolysis research using pine chips, the bio-oil yield was 28% with an operating temperature of 300-500°C without using a catalyst [3]. However, under the temperature lower than 500°C, the bio-oil yield has decreased [11]. The operating condition of temperature will affect the amount of bio-oil yield obtained. In a certain period of time the results of bio-oil are also influenced. The appropriate temperature and time range is needed to get the maximum amount of bio-oil yield. In the temperature range from 200 to 500°C will affects the value of the activation energy that affects the bio-oil results obtained [12, 13]. With the temperature variations in the pyrolysis process, it is expected that pine fruit can produce high-yield bio-oil [14]. The use of temperature in the pyrolysis process must be adjusted to the pyrolysis time of the biomass. The residence time of the pyrolysis process increases the amount of bio-oil obtained.

Biochar in the form of a black solid. Cracked by the pyrolysis process to produce biochar, it is necessary to do a slow pyrolysis process. The slow pyrolysis process will convert carbon for a long time in the temperature around 400°C, so that the yield of biochar is large. Biochar can also be used as fuel and fertilizer for plants because there is still a lot of carbon content.

2. EXPERIMENTAL

2.1 Materials

Pine fruit was obtained from PT. Perhutani, Pujon, Malang. Natural zeolite was obtained from South Malang. Nitrogen gas was obtained from PT. Aneka Gas Industri, Sidoarjo. The chemical used was concentrated hydrochloride acid (HCl 37%), ammonium chloride (NH₄Cl), ammonium molybdate tetra hydrate ((NH₄)₆Mo₇O₂₄·4H₂O) and nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O).

2.2 Pine Fruit Preparation

The pine fruit was sun-dried, crushed and then sieved to the size of -80/+100 mesh. The result, the pine fruit powder, was then oven-dried at a temperature of 110°C. Pine fruit powder was dried until below 5% moisture content.

2.3 Preparation of Ni/Mo/Zeolite Catalyst

Natural zeolite was crushed and sieved using -80/+100 mesh sieve, then zeolite delamination process was carried out.

Natural zeolite (approximately 200 gr) was refluxed and stirred in 1000 mL HCl solution (6 N) for 30 minutes at 50°C. The slurry then filtered and washed until Cl⁻ ion weren't detected by AgNO₃ solution. Then, the cake was dried at 110°C for 3 hours, then dry sample was soaked again in 1000 mL NH₄Cl solution (1 N) at 90°C, while the sample must be stirred for 3 hours every day for one week. The sample was filtered, and the separated cake. Then the cake was washed, and was dried at 110°C for 24 hours as the zeolite catalyst. The next step was impregnation of Mo metal at 3% (w/w) of zeolite catalyst. The zeolite catalyst sample was dissolved into 100 mL (NH₄)₆Mo₇O₂₄·4H₂O (molybdenum) solution then it was refluxed and was gently stirred at 90°C for 6 hours. After 6 hours, the solution was evaporated at 110°C to remove water and Mo/Zeolite catalyst was obtained. The Ni metal from Ni(NO₃)₂·6H₂O solution then was impregnated using the same step to obtained Ni/Mo/Zeolite catalyst. Then the Ni/Mo/Zeolite catalyst was analysis using instrument of SEM for determining of the morphologic form and composition of its components.

The next step, Ni/Mo/Zeolite catalyst were activated by calcination, oxidation, and reduction process with tube furnace. Ni/Mo/Zeolite catalyst (40 grams) were calcinated at 500°C for 6 hours by nitrogen gas flow (400 mL/minute). The catalyst was then oxidized at 500°C for 2 hours by oxygen gas flow (400 mL/minute), after that reduced at 400°C for 2 hours by hydrogen gas flow (400 mL/minute).

2.4 Pyrolysis Process

One hundred grams of pine fruit powder was mixed with 3% (w/w) Ni/Mo/Zeolite catalyst in the pyrolysis chamber. The pyrolysis chamber was the bowl made from stainless steel with the capacity around 250 mL. The heat for pyrolysis was fulfilled by the heating mantle of 4,500 watt. The pyrolysis chamber was connected to the bulb condenser. As the cooling medium for condenser was water. The pyrolysis device was assembled and then the pyrolysis process was run at 550°C for 1 hour. During pyrolysis, the gases was flowed out from the pyrolysis chamber and then its majority was condensed as bio-oil, and the rest was non condensable gases. The residue of mass in the pyrolysis chamber was biochar. The experiment was repeated with a variety of temperature at 550, 600, and 650°C and residence time of pyrolysis for 2, 3, and 4 hours.

2.5 Analysis

Biochar heating value was measured using a bomb calorimeter, bio-oil viscosity was measured using an Ostwald viscosimeter, the water content of bio-oil was analyzed using Karl Fisher Coulometric method, and bio-oil flash point was estimated using ASTM D 93-00 method

3. RESULT AND DISCUSSION

3.1 The Effect of Temperature on Bio-oil Yield

Analysis of raw material for pine fruit powder is presented in Table 1.

Table 1: Analysis of raw material of pine fruit powder [8]

Parameter	Quantity (%)	Unit	Method of Analysis
Total moisture	5.89	%Ar	ASTM D 3302-15
Moisture in sample	3.86	%Adb	ASTM D 3173-11
Volatile content	2.64	%Adb	ASTM D 3174-12
Volatile matter	77.48	%Adb	ASTM D 3175-11
Fixed carbon	19.02	%Adb	ASTM D 3173-13

The data in Table 1 presented the composition of biomass (pine fruit powder) before the pyrolysis process was carried out. Biomass is destroyed with a uniform size of -80/+100 mesh, so that the heat transfer that occurs can be comprehended and also expands the surface area of the biomass [15]. The smaller the size of particle of the biomass, the better the heat transfer due to the more surface area of the biomass. Thus for the catalyst used in the pyrolysis process the same size as the size of particles of pine fruit powder. This is done, so that the effectiveness of the catalyst can be maximized along with the pyrolysed pine fruit powder.

Pyrolysis of pine fruit powder produces bio-oil products. In this study, the catalysts were used to increase the amount of bio-oil obtained in the temperature range of 550-650 C for 1-4 hours. The catalyst used is a modification of natural zeolite by impregnating of Ni and Mo metals. Modification of the catalyst obtained with a new characteristic catalyst called the catalyst Ni/Mo/Zeolite. The pyrolysis of pine fruit resulted under various conditions of temperature and residence time are presented in Figure 1.

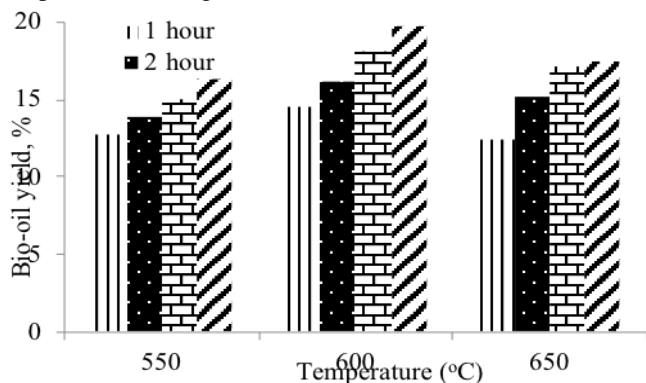


Figure 1: The effect of temperature to bio-oil yield for various residence time using Ni/Mo/Zeolite catalyst

From Figure 1 it can be seen that the bio-oil yield increased from 550 to 600 °C by 12.71 to 19.69%. In this case study, the experiment is based on Arrhenius's law that at the higher of the temperature, the catalyst activity increases [16]. However, different things with the conditions of temperature from 600 to 650 °C, the yield of bio-oil has decreased by 19.69% to 12.36%. It shows that catalyst activity decreases in certain temperature range because of the suffer from damage of the at 650°C. Pyrolysis of pine fruit powder with natural zeolite catalyst which is physically activated, the pyrolysis temperature of 500 °C with 5 grams of catalyst for 200 grams of pine powder achieved the highest yield of bio-oil by 8.1% [8]. It is also influenced by the presence of active metals Ni and Mo which can doubled the bio-oil yield. The presence of temperature is to provide the heat needed for biomass decomposition and fragmentation.

The reaction of cracking of pine fruit powder at higher temperatures from pyrolysis vapors and secondary decomposition of charcoal that occurs, will increasing the yield of uncondensed gas products and then reducing the yield of bio-oil [9], [17]. In this study, the Ni /Mo/Zeolite catalyst was used at 3% of the mass of biomass (100 gr), the temperature condition of pyrolysis at range of 550-650 C, there was an optimum temperature limit at 600oC to produce high bio-oil yields and above 600oC temperature will decrease yield of bio-oil. The catalyst used experienced temperature degradation so that the catalyst mass limit used in this study reached its optimum at a temperature of 600oC. The added catalyst helps draw out the bio-oil contained in the pine fruit. Catalyst activation process before pyrolysis is needed because it will increase the effectiveness of the catalyst.

3.2 The Effect of Time on Bio-oil Yield

The pyrolysis process is carried out with the variety of residence time of 1, 2, 3, and 4 hours. With the variety of residence time be obtained the results that the longer the time of pyrolysis, the greater the yield of bio-oil obtained. It can be seen from Figure 1, with operating conditions temperatures between 550 to 650oC obtained the yield of bio-oil which are increased in a long residence time. It seen from the length of time of pyrolysis at any temperature will increase the yield of bio-oil continuously [1, 5, 18]. In the pyrolysis process carried out at a temperature of 550 to 650 C for 1 to 4 hours obtained bio-oil density of 0.83 to 0.94 gr/ml. bio-oil density ranges lower than 1 gr/ml which affects the quality of bio-oil for use as an alternative fuel. The density of the bio-oil obtained is close to the quality of the bio-oil used as an alternative fuel.

The presence of Ni/Mo/Zeolite catalyst helps to increase bio-oil yields and also increases the bio-oil density [15]. The viscosity obtained from the pyrolysis results in this process is 1.42 to 1.48 cSt, that the bio-oil should be mixed with the other lower viscosity liquid fuel before using it as an alternative fuel. Mixing bio-oil with a lower liquid viscosity

was needed, so that the combustion of bio-oil was easier. The heating value of the bio-oil result of this study ranges from 7,600 to 8,300 cal/gr. Compared to the results of research using pine seeds, the heating value of 5,000 cal/gr was obtained [2], [19], from the research that has been carried out that the heating value has reached the higher heating value.

3.3 The Effect of Time on Bio-oil Yield

The second product of pyrolysis process using a Ni/Mo/Zeolite catalyst at 550, 600, 650°C for 1, 2, 3, and 4 hours was biochar as presented in Figure 2 below.

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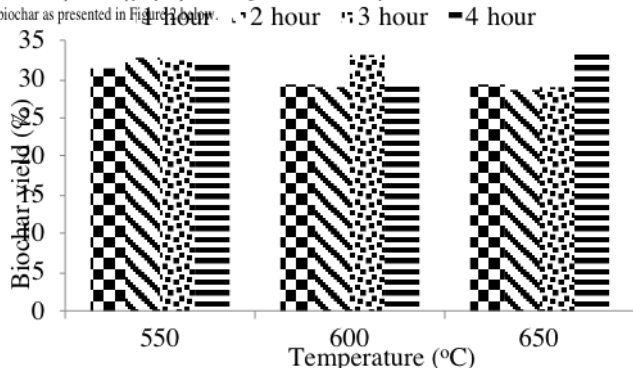


Figure 2: The effect of temperature to biochar yield for various residence time using Ni/Mo/Zeolite catalyst

The product of biochar at the highest bio-oil yield of 650oC for 4 hours, then was analysed its characteristics and was presented in Table 2 below.

Table 2: Analysis of biochar produced from pyrolysis of pine fruit powder

Parameter	Quantity (%)	Unit	Method of Analysis
Heating value	6.825	Cal/gr ,db	ASTM D 5865-13
Moisture in sample	2.93	%adb	ASTM D 3137/D3173-17 A
Ash content	15.14	%adb	ASTM D 3174-12
Volatile matter	5.96	%adb	ASTM D 3175-17
Fixed carbon	75.97	%adb	ASTM D 3172-13

In figure 2 can be seen that yield of biochar is 28 to 33% at temperature 550-650oC. This affects the pyrolysis process, that by doing slow pyrolysis, the desired biochar results will have a large yield value. Long residence time of pyrolysis process will result in highest yield of biochar. Biochar which still contains a lot of carbon can still be used as fuel or as plant growing media. Biochar is mostly used by Indonesian people

for fertilizer, while the results of pyrolysis are not just wasted. Based on Table 2, the biochar with highest yield of bio-oil result has moisture content in sample 2.93% adb where heating value result of 6.400 to 6.760 Cal/gr. Under conditions of higher operating temperature and time, the mass value and heating value of biochar will decrease. This is due to the carbon degradation found in the biomass (pine fruit) used. Carbon content in the biomass will degrade with increasing temperature and heating time. The highest of the temperature and the longer the residence time of pyrolysis will be affects the carbon and causes the biochar heating value and mass to decrease [13, 20]. Other energy investigation can be further considered for further research and integration [21] [22].

4. CONCLUSION

From the result of the study, it can be concluded that the pyrolysis process produces high bio-oil yields as the temperature increases until an optimum temperature of 600oC is obtained. The maximum bio-oil yield in the pyrolysis process with temperature conditions of 600oC for 4 hours was 19.69%. The condition of the pyrolysis pine operating temperature with Ni/Mo/zeolite catalyst with a duration of 1, 2, 3, and 4 hours experienced a continuous increase in the yield of bio-oil. The density of bio-oil is 0.83 to 0.94 gr/mL and the heating value is 7,600 to 8,300 Cal/gr. The yield of biochar obtained was 28 to 33% with a calorific value of 6,400 to 6,760 Cal/gr. The results of pyrolysis are utilized in the form of bio-oil which is used for alternative fuels, while biochar is used for fuel or plant growing media. The viscosity of bio-oil was ranging from 1.42 to 1.48, then the bio-oil needs to be mixed with a low viscosity liquid fuel, so that bio-oil can be used as a renewable alternative fuel.

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