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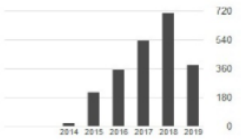

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Kinetic Studies of Pyrolysis of Pine Fruit with Reaction First Orde Model

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ABSTRACT

The results of the pyrolysis of pinecone seeds in the form of oil, gas and char can be used as fuel but can also be used as raw material for the chemical industry. In order to facilitate learning in the application of pinecone seeds, a kinetic model can be used to predict biochar, biooil, and biogas produced from the pyrolysis process. Pyrolysis Process is one hundred grams of pine fruit were mixed with 3% (m/m) catalyst in the pyrolysis reactor. The pyrolysis device was assembled and then the pyrolysis device was run at 500^{o}C for 1 hour. The experiment was repeated with a variety of temperature at 500, 550, 600, and 650^{o}C and duration time of pyrolysis for 1, 2, 3, and 4 hours. Research using Ni/Mo/NZA and Mo/bentonite catalysts. In this model, pinecone is decomposed into vapor, liquid (biooil), and solid (biochar). The one-step reaction model describes the pyrolysis reaction as a first order reaction. Yield obtained based on the reaction kinetics model: Ln (1 – Y) = A.exp((E/R)/T).t. From the results of data processing prices A = 1 and E/R between -1092.83^{0}K to -5225.42^{0}K Yield eror between 4.05% to 8.55%

Keywords: pinecone, pyrolysis, catalyst, yield.

INTRODUCTION

Fruit seeds in pine plants can be used as raw materials for the chemical industry to be processed into energy sources. So that the potential for pine plants as a source of energy is very large. Pinecone seeds when used as fuel, apart from having a low calorific value, can only be used as solid fuel, therefore, in order to have a high calorific value and can be used as solid, liquid, and gas fuels, it is carried out by the pyrolysis process. The results of pyrolysis in the form of oil, gas and char besides being used as fuel can also be used as raw materials for the chemical industry. In order to facilitate learning in the application of pinecone seeds, a kinetic model is needed that can be used to predict biochar, biooil, and biogas produced from the pyrolysis process.
The kinetics of pyrolysis has been studied a lot but interpretations of research data vary, this is due to various types of raw materials and sizes, complex material compositions, reactor shapes, methods and process conditions For materials with complex and heterogeneous compositions, the kinetics of prolysis reactions approached by the speed of formation of results in terms of the maximum results obtained. (Prakash, 2008). From previous studies, the reaction in pyrolysis tends to follow the first order reaction of the Arrhenius method

MATERIAL AND METHOD

Materials

Pine fruit was obtained from Malang. Indonesia. Natural zeolite was obtained from South Malang. The chemical used was Nitrogen gas, sulfuric acid (H_2SO_4 98%), Barium Chloride ($BaCl_2$), dan ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$). The catalysts used are Ni/Mo/NZA and Mo/bentonite

Literature review

Modeling the reaction in this pyrolysis process to get the value of the kinetic parameters. The method used is Simple Arrhenius Modeling. The Arrhenius method is a simple method for modeling the pyrolysis process. The equation is a one-step reaction
The one-step reaction model describes the pyrolysis reaction as a first-order reaction (Prakash, 2008). In this model, pinecone is decomposed into biogas, biooil, and biochar.
The reaction model is a one-step model, with parallel reactions:

A → B

A → C

A → D

With A : pinua fruit seeds

B : Biogas
C : Biooil
D : Biochar

The equation model for the reaction rate can be expressed as:

$r = k \cdot (1 - Y)$ (1)

$k = A.\exp((E/R)/T)$

r = rate of reaction, % mass
k = reaction rate constant, 1/min
Y = yield, %mass
A = collision frequency factor
E = activation energy, J/mol
R = ideal gas constant, J/mol0K
T = temperature, 0K

equation (1) can be changed to

$\frac{d(1-Y)}{dt} = A.\exp(\frac{E/R}{T}).(1 - Y)$ (2)

d = differential
t = time, minutes

equation (2) can be changed to

$\frac{d(1-Y)}{(1-Y)} = A.\exp(\frac{E/R}{T}).dt$

$\int_0^Y \frac{d(1-Y)}{(1-Y)} = A.\exp(\frac{E/R}{T}).\int_0^t dt$

$Ln\,(1 - Y) = A.\exp(\frac{E/R}{T}).t$ (3)

Equation (3) is used to find the values of A and E/R with least square

Method

Pine Fruit Preparation

The pine fruit was sun-dried, crushed, and then sieved to the size of -80/+100 mesh. The result was then oven-dried at a temperature of 110^{o}C.

Pyrolysis Process

One hundred grams of pine fruit were mixed with 3% (m/m) catalyst of Ni/Mo/NZA in the pyrolysis reactor. The pyrolysis device was assembled and then the pyrolysis device was run at 500^{o}C for 1 hour. The experiment was repeated with a variety of temperature at 500, 550, 600, and 650^{o}C and duration time of pyrolysis for 1, 2, 3, and 4 hours. The experiment was repeated again with catalyst of Mo/bentonite

RESULTS AND DISCUSSION

Result

The pyrolysis process of pinecone biomass uses a fixed bed reactor with the slow pyrolysis method. The pyrolysis process was carried out using 100 grams of pinecone feed with a particle size of 80 to 100 mesh. This

process was carried out for pyrolysis temperatures of 500^{0}C, 550^{0}C, 600^{0}C, and 650^{0}C (Grierson., 2009). This research is to obtain biooil yield and biochar yield data. Experimental data shows the formation of more and more biooil yields and biochar yields. The data from the pyrolysis of pinecone measurements are shown in table 1 and table 2.

This data is used to obtain the parameters in equation (3) which is a model of the pyrolysis velocity of pinecone. The biomass used is dry pinecone powder. The results of the equation simulation are then compared with the research data. The data in table 1 is clarified with pictures 1 and 2 and the data in table 2 is clarified with pictures 3 and 4

Table 1. The relationship between the yield of biochar and biooil using Ni/Mo/NZA . catalyst

Temperatur (^{0}C)	Time (minute)	Experiment			Mlodeling	
		Biooil density (g/mL)	Biooil yield	Biochar yield	Biooil yield	Biochar yield
500	60	0.8224	0.0725	0.095	0.0722	0.098
	120	0.8582	0.14	0.018	0.13	0.2052
	180	0.8878	0.2022	0.2587	0.2042	0.26
	240	0.8872	0.262	0.329	0.2622	0.3212
550	60	0, 9111	0.0852	0.1032	0.0711	0.1122
	120	0,9267	0.1613	0.1957	0.16	0.2282
	180	0,9423	0.23	0.2786	0.2255	0.285
	240	0,9578	0.2882	0.353	0.2912	0.3211
600	60	0,9683	0.102	0.11	0.105	0.1232
	120	0,9982	0.19	0.2077	0.1771	0,2092
	180	0.9506	0.2715	0.2948	0.2782	0.296
	240	0,9843	0.3445	0.3723	0.3363	0.3124
650	60	0,9511	0.1215	0.1156	0.1233	0.1293
	120	0,9390	0.2282	0.2178	0.2192	0.2282
	180	0,9492	0.322	0.3082	0.327	0.2882
	240	0,9682	0.4044	0.3882	0.3973	0.3333

Biooil yield error = 4.67%
Biochar yield error = 7.65 %

Table 2. The relationship between the yield of biochar and biooil using Mo/Bentonite . catalyst

Temperatur (^{0}C)	Time (minute)	Experiment			Modeling	
		Biooil density (g/mL)	Biooil yield	Biochar yield	Biooil yield	Biochar yield
500	60	0.8407	0,099	0,1053	0,099	0,1053
	120	0.8482	0,1884	0,2	0,1884	0,1874
	180	0.878	0,2688	0,2838	0,2688	0,2777
	240	0.8816	0,3413	0,3593	0,3413	0,3388
550	60	0.9598	0,116	0,113999	0,116	0,1222
	120	0.8958	0,2186	0,212694	0,2186	0,2222
	180	0.8993	0,3093	0,301421	0,3093	0,313
	240	0.9149	0,3894	0,38	0,3895	0,388
600	60	0.97980	0,1257	0,1164	0,1257	0,1177
	120	1.0131	0,2356	0,2192	0,2356	0,2792
	180	0.8696	0,3317	0,31	0,3317	0,3333
	240	0.9930	0,4157	0,3903	0,4157	0,4133
650	60	0.9660	0,1492	0,1232	0,1492	0,1553
	120	1.0153	0,2762	0,2312	0,2762	0,2882
	180	1.0153	0,3842	0,3259	0,3842	0,3834
	240	1.0349	0,476	0,409	0,476	0.4844

Biooil yield error = 4.05%

Biochar yield error = 8.55 %

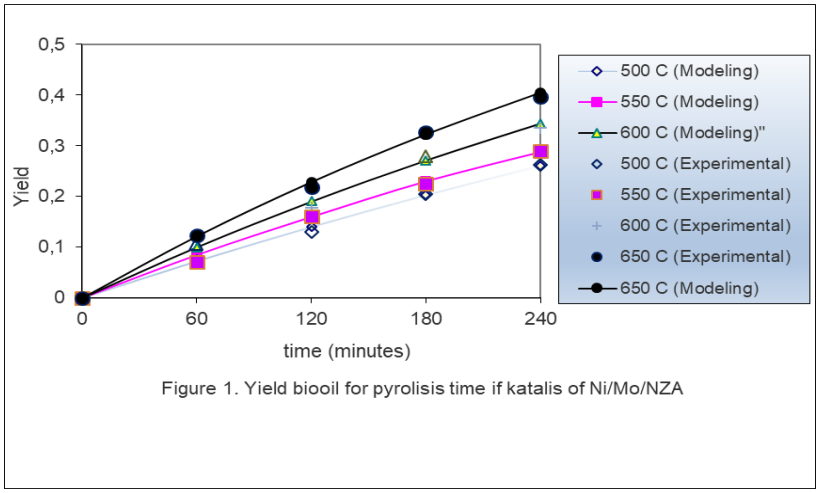

Figure 1. Yield biooil for pyrolisis time if katalis of Ni/Mo/NZA

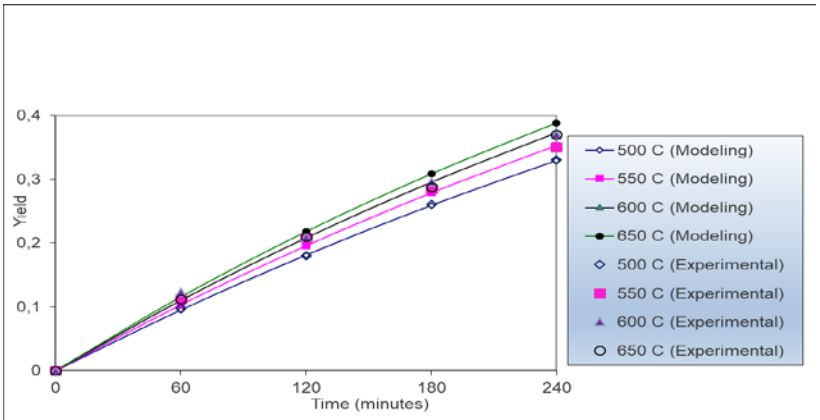

Figure 2. Yield biochar for pyrolisis time if katalis of Ni/Mo/NZA

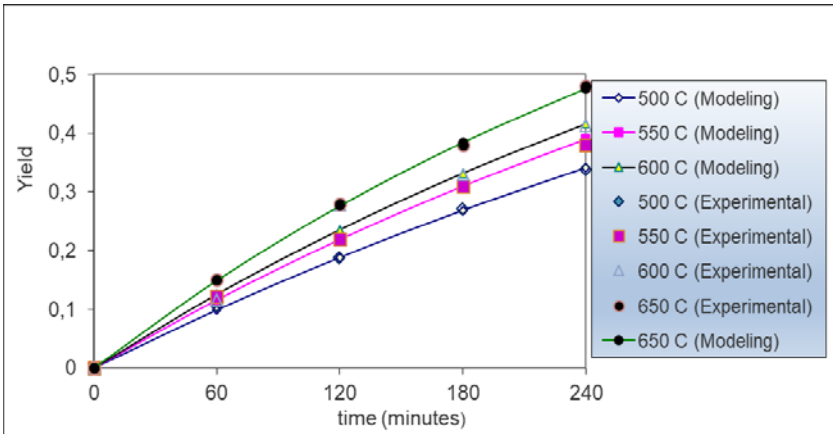

Figure 3. Yield biooil for pyrolisis time if katalis of Mo/bentonit

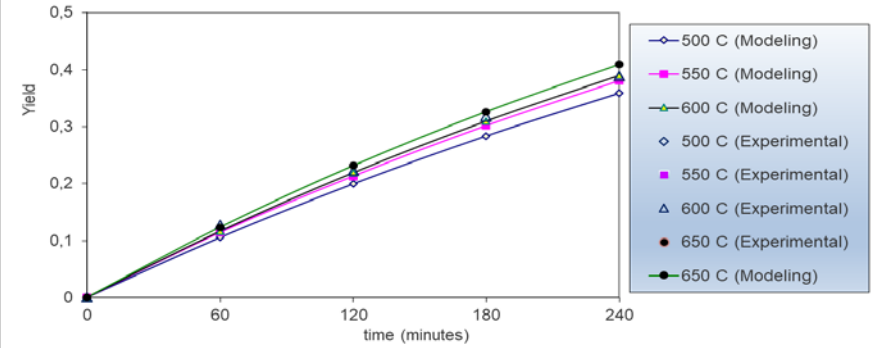

Figure 4. Yield biochar for pyrolisis time if katalis of Mo/bentonit

The results of the reaction rate equation model obtained are
Equation of reaction rate using catalyst of Ni/Mo/NZA
For biooil :

$-r = k_{O1} . (1 - Y_{O1})$ with $k_{O1} = exp(-5536{,}88/T)$

For biochar :

$-r = k_{C1} . (1 - Y_{C1})$ with $k_{C1} = exp(-5309{,}74/T)$

Equation of reaction rate using catalyst of Mo/bentonite

For biooil :

$-r = k_{O2} . (1 - Y_{O2})$ with $k_{O2} = 0{,}0022.exp(-1014{,}88/T)$

Fotr biochar :

$-r = k_{C2} . (1 - Y_{C2})$ with $k_{C2} = exp(-4876{,}3/T)$

Equation to get yield using catalyst of Ni/Mo/NZA :
For biooil :

$$\text{Ln}\,(1 - Y_{O1}) = 0.0025.\exp\left(\frac{-1092.83}{T}\right) . t$$

Forhar :

$$\text{Ln}\,(1 - Y_{C1}) = \exp\left(\frac{-4971.2}{T}\right) . t$$

Equation to get yield using catalyst of Mo/Bentonit :

For biooil :

$$\text{Ln}\,(1 - Y_{O2}) = 0.0022.\exp\left(\frac{-5132}{T}\right) . t$$

For biochar :

$$\text{Ln}\,(1 - Y_{C2}) = \exp\left(\frac{-5225.42}{T}\right) . t$$

Discussion

In the pyrolysis process there are three main areas in the thermal decomposition process, namely the dehydration zone, the degradation zone, and the charcoal formation zone (Wang S., 2011). The dehydration zone is located between 100-150^{0}C. In this zone there is a process of removing water content in the biomass. The second zone is a degradation zone that takes place at a temperature of 200-600^{0}C. In this zone there is a reduction in mass because there is a process of degradation of organic compounds in pine seeds, namely cellulose, hemicellulose and lignin.

The rapid rate of mass reduction takes place at a temperature of 300-800^{0}C which is the temperature range for the process of degradation or breakdown of organic compounds found in pinecone feed, namely cellulose and hemicellulose. Cellulose degradation takes place at a temperature of 200-390^{0}C, hemicellulose degradation takes place at a temperature of 150-350, and lignin degradation takes place at a temperature of 380-800^{0}C (Collard, 2014). This temperature difference is caused by differences in the structure and content of the cellulose, hemicellulose and lignin components. The heating rate has no effect on the biomass degradation profile (Wijayanti W., 2019). The heating rate affects the thermal energy during the pyrolysis process so that it only affects the initial and final temperatures of the degradation process of cellulose, hemicellulose and lignin components. Each degradation reaction breaks down the components of cellulose, hemicellulose and lignin into compounds with lower molecular weights. Cellulose produces 5-15% water, hemicellulose produces 20-30% water, and lignin produces 8-15% water (Collard, 2014). The process of forming H2O components in cellulose is caused by the depolymerization process due to intermolecular reactions during the decomposition process, the formation of H2O components from hemicellulose is the breaking of xylan ring bonds, lignin produces H2O from breaking bonds in lignin (Collard, 2014). After the degradation process, each component of the biopolymer undergoes charcoal formation at a temperature of 500-800^{0}C which is the process of forming and combining benzene rings in a polycyclic structure. During this process, water and non-condensable gases are released. So high temperatures increase the water content in bio oil because each series of reactions occurs at high temperatures and is followed by the release and formation of water compounds (Jelita, 2018).

Figures 1 to 4 show characteristic analyzes for biochar and biooil. The graph shows that the higher the pyrolysis time, the higher the yield of biodiesel and biochar. The increase in biooil yield is caused by a decrease in the acid number which indicates a reduction in the fatty acid content in bio oil (Wijayanti W., 2019). This is an indicator that the increase in pyrolysis temperature affects the distribution of compound content in bio oil. This tendency is because at high temperatures there is a breakdown of compound chains which causes the composition of the components in the product to differ, thus affecting the mass of the molecules that make up the substance. The results of the analysis show that the density of bio oil produced is closer to the density of water (1 gr/ml) than the density of biodiesel fuel (0.87 gr/ml). This shows that at high temperatures, bio oil still contains water with a fairly high percentage.

At high temperatures, side reactions occur which cause stretching of the bonds in the molecule, besides that high temperatures cause water products to increase, thereby reducing viscosity (Wijayanti W., 2019). During the pyrolysis process there is a breakdown of the main constituent structures of biomass, namely cellulose, hemicellulose and lignin. According to (Uddin et al., 2014) these three components are degraded based on the following reaction:

a. Cellulose Degradation → Levoglucosan → $C_2H_4O_2$ + $C_2H_2O_2$ + CH_3CHO + C_3H_6O + CO_2 + CO + CH_4 + H_2O + 5-hydroxymethyl-furfural + Charcoal
b. Hemicellulose Degradation Hemicellulose → Xylos → H_2 + H_2O + CO + CO_2 + CH_2O + CH_3OH + C_2H_5OH + Charcoal
c. Lignin Degradation $C_{11}H_{12}O_4$ (Lignin) → Para-Coumaryl + Phenol + H_2 + H_2O + $C_3H_4O_2$ + CO + CH_4 + C_2H_4 + Charcoal

The high temperature causes the composition of solid biomass compounds to turn into liquid and gaseous compounds. The decomposition of each of these compounds causes the solid biomass to decompose into liquid and gas. This is what causes the graph of the increase in yield at high temperatures, because the biomass elements in the form of hemicellulose, cellulose, and lignin are decomposed simultaneously. In the presence of hemicellulose, cellulose, and lignin decomposed simultaneously, the yield changes become slower (Wijayanti, 2019). Therefore, the change of pinecone into biochar cannot be detected, it can only be seen at the end of the pyrolysis process, the solid yield is already in the form of char. However, the mechanism of biomass decomposition in the pyrolysis process is in accordance with the results of the data in this study. The pyrolysis process produces water and several compounds that occur simultaneously with reactions that produce gas, char, and tar. The hydroxyl groups in cellulose are converted to water, char, and tar.

CONCLUSION

1. The pyrolysis process is divided into three parts, namely the dehydration process, the decomposition of lignucellulose, and the formation of charcoal.
2. The longer the pyrolysis time, the higher the yield of bio oil and biochar
3. The higher the pyrolysis temperature, the higher the yield of bio oil and biochar
4. The use of Mo/bentonite catalysts produces higher yields of biooil and biochar than the use of Ni/Mo/NZA katalis catalysts
5. The use of Mo/bentonite catalyst has a smaller error than the use of Ni/Mo/NZA . catalyst

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