Study of Reaction Kinetics by Flynn Wall Ozawa Method on Sawdust Pyrolysis Process

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ABSTRACT

Pyrolysis, also called thermolysis, will chemically decompose organic matter (biomass) through a heating process without or little O_2 or other reagents, where the raw material will undergo a breakdown of the chemical structure into a gas phase. The purpose of this study is to know the amount of activation energy calculated using the Flynn Wall Ozawa method. The biomass used is Dutch teak sawdust obtained from the wood furniture industry in the Tangerang area. The experimental results of pyrolysis of Dutch teak sawdust with certain heating rate have obtained bio crude oil (BCO) as much as 6.00%, 6.50%, 6.83%, 7.33%, 7.67%, 8.83%, 10.17%, 14.33%, 16.33%. While the results of the round gas opening, BCO has been obtained as much as 5.67%, 6.17%, 6.67%, 7.17%, 7.33%, 7.83%, 9.67%, 13.83%, 15.83%. The pyrolysis process produces three types of products, which are solid product or char, bio crude oil (BCO) and bio gas. In our research, the best quality BCO was obtained at temperatures from 548 K to 598 K. The BCO obtained at this temperature is brownish yellow, with an average mass of about 48 g. Temperature optimum for production BCO is 673 K with kinetics parameter for BCO are Ea=3587.85 kJ/mol, A=3.73 min^{-1}, bio gas Ea=3750.21 kJ/mol, A=2.97 min^{-1}, and char Ea=6183.42 kJ/mol, A=1.00 min^{-1}.

1. INTRODUCTION

1.1 Preliminary

Fuel consumption in Indonesia has exceeded domestic production since 1995. Within the next 15 – 20 years, the reserve of Indonesia's petroleum is estimated to be running out. This estimate is proven by there is often a shortage of fuel in several regions in Indonesia. (Hambali E et al., 2006).

It is projected that by 2050 the world's fossil energy reserves will be exhausted. In addition, gasoline which is fossil fuel will one day run out too. Therefore, fossil fuel is not a sustainable energy source. To build sustainable energy security, it is needed to switch to the use of sustainable energy sources to the renewable ones, low in greenhouse gas emissions, and based on domestic resources so as not to depend on other countries.

One of the alternative energies that has been widely developed is organic matter (biomass). Biomass can come from plantation or agricultural crops, forests, livestock or even garbage. Due to the hydrocarbon content of its compounds, biomass can be used to provide heat, produce fuel, and generate electricity. One of the biomass that is found is waste from Dutch teak powder which comes from the wood processing industry. In Dutch teak wood powder, there are substances that can be decomposed during the pyrolysis process (Sukadaryati et al., 2005).

These substances consist of cellulose, hemicellulose and lignin. To produce high quality char products, the slow pyrolysis method is used. In

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the slow pyrolysis method, the heating rate used is very slow so that the gas and tar produced are low. On the other hand, the curing process of the slow pyrolysis method is very high. One of the parameters that affect the quality of the pyrolysis char product is temperature. If the temperature is increased, the molecules in the biomass have an energy level (Mohan El Al., 2006).

Pyrolysis technology was developed with a variety of methods for clean technology and had an aspect of utilizing natural resources. Pyrolysis process uses a large amount of energy to break down the chemical elements in the pyrolysis material into small molecules and a gas phase. This conversion process is targeted to obtain BCO. The reaction rate of biomass to form BCO is very specific and needs to be calculated to be used as a basis for reactor design. Therefore, it is necessary to calculate the energy consumption, including heating rate, temperature, mass and particle size of the material, kinetic parameter data, especially activation energy, which is the basis for determining the sensitivity level of biomass.

In 1899 the Swedish chemist Svante Arrhenius combined the concept of activation energy and Boltzman's law of distribution into one of the most important equations in the world of physical chemistry, the Arrhenius equation, (Goncalves, RFB et al., 2013).

$$K = A \cdot e^{\frac{Ea}{RT}} \qquad (1)$$

Based on the equation, to determine the reaction rate constant (k), the activation energy value (Ea) and the pre-exponential factor (A) are required. Ea and A are commonly referred to as kinetic parameters. Determination or estimation method of kinetic parameters (E and A) is the core of various studies on kinetics (Goncalves, RFB et al., 2013).

One of the reaction kinetics methods used to calculate the value of activation energy (Ea) and pre-exponential factor (A) is the Flynn Wall Ozawa method. Flynn Wall Ozawa's approach required the sample to be heated at a minimum of three different temperature rise rates. The isoconversional integral method suggested independently by Ozawa, Flynn and Wall using Doyle's estimate of the temperature integral, assume that g(α) is a constant conversion rate and after using Doyle's estimate the result of the logarithmic integration is

$$\text{Log} = \left(\log\left(\frac{AE}{g(a)R}\right) - 5.331 - 1.052\frac{E}{RT}\right) \qquad (2)$$

The activation energy can be determined by the slope of the plot line obtained from several heating/temperature rise rates. Meanwhile, the value of the pre-exponential factor can be determined through the value of the linear plot constant (c). The Flynn Wall Ozawa method provides different values of activation energy and pre-exponential factors for each conversion, (Bawase, MA et al., 2012).

2. EXPERIMENTAL PART

2.1 Material:

The material used in this research is waste biomass from Dutch teak sawdust obtained from the wood furniture industry in the Tangerang area.

2.2 Method

2.2.1 Biomass Pyrolysis Process

Pyrolysis was carried out on a simple device designed with a capacity of 600 g of sawdust biomass. 600 g of sawdust was put into the pyrolysis reactor tube. The reactor tube was then inserted into the combustion chamber. A funnel equipped with a thermocouple was installed above the reactor tube to measure the combustion temperature which is connected to a temperature information thermometer.

The temperature is set according to predetermined variables, starting from 473 K, 498 K, 523 K, 548 K, 573 K, 598 K, 623 K, 648 K, and 673 K with heating rate and observations at the time intervals for 5, 10, and 15 minutes after the specified temperature was reached. It was also recorded how long it took until the pyrolysis process was completed, which was marked by the absence of dripping BCO. The BCO yield obtained was measured and compared at each temperature and time change that has been set previously.

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2.2.2Variables

This research was carried out with the temperature adjusted according to predetermined variables.

3. RESULTS AND DISCUSSION

3.1 BCO Yield Comparison

The experimental results of pyrolysis of Dutch teak sawdust. The higher the temperature, the higher the BCO yield. The color of the BCO, the higher the temperature, the darker it will be. The higher the temperature reached, the less the remaining charcoal will be because the combustion occurs more evenly. From the results above, the density of each sample can be calculated. The density formula itself is = m / v.

The lowest BCO yield (Fig. 3.1) was in the 1st experiment and the highest BCO yield was in the 9th experiment. From experiments 1 to 9 obtained BCO as much as 5.67%, 6.17%, 6 ,67%, 7.17%, 7.33%, 7.83%, 9.67%, 13.83%, 15.83%. The higher the temperature, the higher the BCO yield. The color of the BCO becomes darker with the increase in temperature. The higher the temperature reached, the less the remaining charcoal will be because the pyrolysis occurs more evenly.

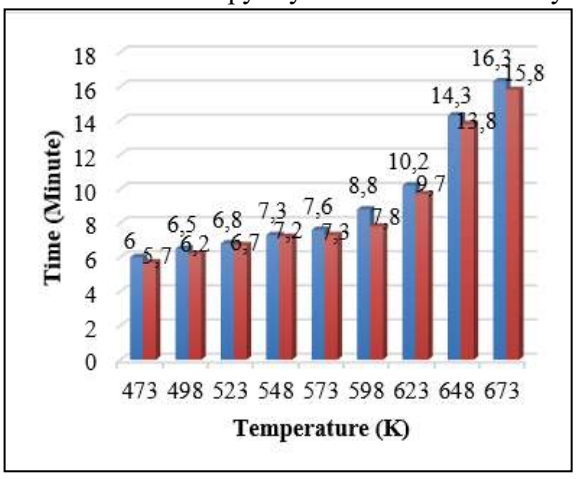

Figure 1 Effect of heating rate on the formation of BCO.

3.2 Heating Rate

Heating rate (Fig.3.2) of BCO was obtained at a temperature of 473 K to 673 K at gas cycles and ranged from 0.763 to 0.989 g/cm^3. There are specific differences in sample 7, Point number 0.76 for round gas opening and 0.95 for round gas opening.

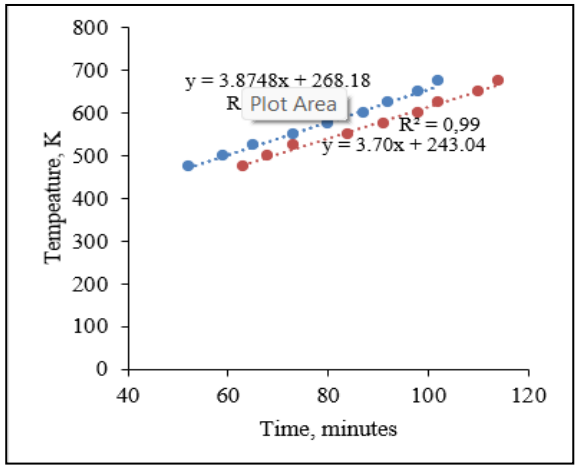

Figure 2 Slope of Temperature vs time

3.3 Flyn Ozawa Method Equation

Replace the initial mass with CA_0 to derive the data into the Fllyn wall Ozawa method equation.

$$\frac{dCA}{dt} = -K.C_A \qquad (3)$$

Where X is the mass conversion, where $X=\frac{m_o-m_t}{m_o}$

and $\frac{dT}{dt} = \beta$, then enter into Eq. (3)

$\beta.\frac{dCa0(1-X)}{dT} = -K.C_{A0}(1-X)$ then input the fraction to each component.

$$\ln(\beta)=\ln\left(\frac{A.Ea}{R.(-\ln(1-X))}\right)-5.331-1.052\frac{Ea}{RT} \qquad (4)$$

from Eq. (4) we get the slope $-1.052\frac{Ea}{RT}$ and intercept $\ln\left(\frac{A.Ea}{R.(-\ln(1-X))}\right)-5.331$.

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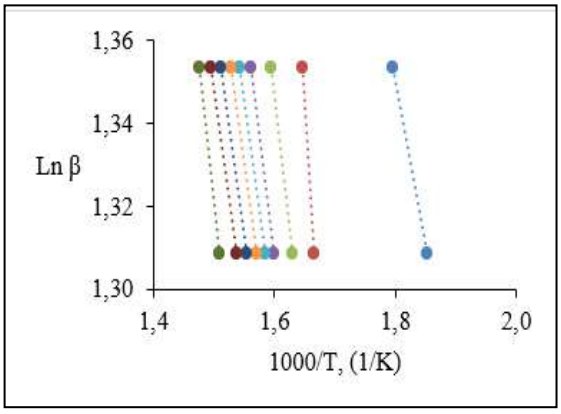

Figure 3 Flynn Wall Ozawa chart

At 32% mass conversion, the equation from Figure 3.3 the Slope value = - 0.80 and Intercept = 2.86, after that calculate the value of Ea with equation slope.

$$-0.80 = -1.052 \frac{Ea}{(8.314).(524)}$$

$$Ea = \frac{(8.314).(524).(-0.80)}{-1.052}$$

Ea = 3314 kJ/mol.

Then calculate the value of A with equation intercept.

$$2.86 = \ln\left(\frac{A.(3314)}{R.(-\ln(1-x))}\right) - 5.331$$

$$\exp(2.86 + 5.331) = \frac{A.(3314)}{(8.314)\ (0.39)}$$

$$A = \exp(8.191)\left(\frac{(8.314).(0.39)}{3314}\right)$$

$$A = 3.49\ min^{-1}.$$

The following is the result of the calculation of Ea and A from each experiment. In Table 1 it can be seen that each calculation result of Ea and A values are different. The factors that influence the difference between the values of Ea and A include the value of X (conversion), temperature and heating rate.

Table 1 Calculation of activation energy (Ea) and A

Conversion (X)	Q, Average	-LN(1-X)	Ea, kJ/mol	A, min^{-1}
32	524	0.39	3314	3.49
34	540	0.42	4567	4.28
36	562	0.45	3154	3.24
38	584	0.48	3926	3.37
40	591	0.51	3084	3.33
42	596	0.54	3107	3.46
44	600	0.58	3130	3.61
46	605	0.62	3154	3.78
48	609	0.65	3178	3.94
50	623	0.69	5265	4.78
52	643	0.73	10160	10.63
54	661	0.78	28064	604.13

4. CONCLUSION

The best quality BCO was obtained at a temperature of 498 K to 578 K. The results obtained at this temperature are brownish yellow, with an average volume of ± 48 g of BCO (52.6 ml).

In this study, two heating rates were used. The heating rate is obtained from the relationship between the time graph and the temperature. The heating rate value is influenced by how much the gas regulator rotates. At the opening of the regulator gas cycle the value is 3.8 $C.min^{-1}$ and at the opening of the regulator gas cycle the value is 3.7 $C.min^{-1}$. The wider the rotation of the gas regulator, the higher the heating rate. And the higher the heating rate, the faster the reaction temperature rise will be.

In addition to the heating rate, there are other factors that affect temperature pyrolysis. Temperatures will affect the amount of biomass components that are degraded in the pyrolysis process. The higher the temperature, the more the degradation process occurs. A high yield value indicates that the final mass remaining is relatively small (most of the biomass components are converted to BCO, char, and gas. From the heating rate, temperature, and yields data, we get the Flynn Wall Ozawa equation (4).

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And from the heating rate, temperature and yields data obtained by the Flynn Wall Ozawa graph in Figure 3.. From the graph above, the slope and intercept values are obtained by drawing a linear ..

Slope $-1.052\frac{Ea}{RT}$ and intercept $= \left(\frac{A.Ea}{R.(-\ln(1-X))}\right) -5.331$. From the slope and intercept, the value of activation energy (Ea) and A can be seen in Table 1.

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