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Analysis of the Reaction Kinetic of Pyrolysis Process in the Styrofoam Waste by using Catalyst Cu

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Abstract

Styrofoam is one of the biggest contributors to plastic waste. Styrofoam includes polystyrene plastics derived from styrene monomers, which cannot decompose naturally. The method commonly used to process plastic waste is pyrolysis. The purpose of this study is to determine the effect of the number of Cu catalysts on the kinetics of the reaction in the Styrofoam waste pyrolysis process. Based on the research that has been done, the addition of cu catalysts affects the kinetics of the reaction in the pyrolysis process of styrofoam waste. The fastest rate of reaction is a catalyst of 8%, while for the slow rate, the catalyst is 0%. In the catalytic reaction, 10% of the reaction rate is decreased. This is due to the formation of lumps between the catalyst and the styrofoam that makes the catalytic reaction not work optimally.

Keywords: *Cu; kinetic reaction; pyrolysis; styrofoam*

Introduction

Waste is one of the biggest threats facing the world and Indonesia if it is not handled properly. According to the Central Statistics Agency (BPS), every year the population of Indonesia produces 65 million tons of garbage per year or the equivalent of 178,000 tons per day (BPS, 2018). According to Asmara, 12% of the total waste produced is plastic waste, which is equivalent to 22.7 thousand tons per day. Styrofoam waste accounts for 1.14% of the 12% of plastic waste generated every day (Asmara and Kholidah, 2019).

Styrofoam is a plastic type of polystyrene derived from a monomer of styrene. This type of plastic cannot be naturally degraded as organic garbage and is very difficult to degrade by the soil (Kholidah, 2018). This styrofoam is widely used in dining homes, five-foot merchants, and even some cafes as containers for ready-made food. Styrofoam is also used in the electronics industry as a protective packaging material for electronic items because styrofoam has flexible, practical, and easy-to-use properties, which make its use increase (Nanda, 2018).

One of the most common methods used to process plastic garbage is by repairing or using it as a handicraft. However, this recycling process only turns plastic garbage into a new form and does not shrink. Therefore, it requires other methods to handle a lot of plastic waste. One way is to transform plastic waste into alternative fuels through the pyrolysis method (K, Mukhtar et al, 2016).

Pyrolysis is the process of breaking down large molecular polymers into compounds with a smaller molecular weight. According to Nugroho, one of the advantages of the pyrolysis method in the combustion of plastic waste is that it can be done on a closed system that releases no pollutants into the air (Nugroho J and Rahyani E, 2010).

The study of kinetics is a useful approach to predicting raw materials during the thermal decomposition process. Suwandono and Hardianto (2019) researched the influence of pyrolysis temperature on the kinetic rate and volume of tar or oil resulting from pyrolysis on plastic waste. In this study, the kinetics of the reaction can be determined by the Arrhenius equation as long as the total kinetic value of reaction variation at temperature is obtained, that is, the activation energy (Ea) of 25839.08 kJ/mol and the pre-exponential factor (A) value of 427.51 minutes-1.

In the process of pyrolysis, one of the factors that can increase the rate of reaction is the catalyst. Adnan and Jan conducted research by filtering plastic into liquid fuels using four types of catalysts: Cu, Cu-Al_2O_3, Cu-Mmn, and Cu-AC. In this study, the most pyrolysis oil was obtained with the Cu catalyst (93.93%), while for Cu-Al_2O_3, Cu-Mmn, and Cu-AC catalysts, the pyrolyzed oil was obtained at 87%, 89.20%, and 83.47% (Adnan, Shah, dan Jan 2014).

Asmara and Kholidah researched the influence of the number of Zn catalysts on the results of the pyrolysis of styrofoam waste into liquid fuels. This study used catalyst variations of 0, 4, 6, and 8% with a temperature of 250^oC. In this study, the most optimal result for liquid fuel was obtained at a 6% catalyst variation of 49.76%, and the lowest result at an 8% variance of 39.51% (Asmara dan Kholidah, 2019).

Based on several previous studies, the researchers are interested in conducting further research on the kinetic analysis of the pyrolysis process reactions of styrofoam waste using Cu catalysts. Where variations of Cu catalysts are used (0, 4, 6, 8, and 10%), at a pyrolysis temperature of 400^oC, with a time interval of measurement of the oil resulting from the pyrolysis of once in every 10 minutes, and the weight of the waste styrofoam is 250 grams. The use of a temperature of 400^oC is recommended because based on several previous experiments, the temperature is the most optimal for producing a lot of pyrolysis oil. It is a stable catalyst at high temperatures. What distinguishes this study from previous studies using Cu catalysts is the type of plastic, material variation, variation in the amount of catalyst, and temperature used in the pyrolysis process. The study also determined the kinetics of the pyrolysis reaction process of styrofoam waste using the Cu catalyst. Previous research only compared the amount of oil produced from some types of Cu catalysts. The reaction kinetics calculated in this study are activation energy (Ea), pre-exponential factor (A), and the reaction rate constant (k) using the Arrhenius equation.

Methods

Tools and Materials

As for the tools used in this research, they are pyrolysis units, Erlenmeyer, pipet measurement, glass measuring, scissors, analytical balance, funnel, oven, plastic bottle, and watch. The materials used in this study are Styrofoam waste and Cu catalysts. The Cu used in this study was high-purity copper metal powder (7.05 oz), Cas No. 1317-33-5, EINECS-Nr 231-159-6, and grain size 0.071 mm with an impurity content of 99.5%. The researcher bought this product at the Laboratory of Politeknik Akamigas, Palembang.

Work Procedure

Materials Preparation

Before the process of pyrolysis, the raw materials of styrofoam are first cleaned with water and then naturally dried using sunlight. After the drying process, the raw material used is reduced to a size of ± 2-3 cm and then weighed as much as 250 gr, according to the study variables.

Catalyst Activation

In this study, Cu was used as a catalyst where Cu was activated before being used in the pyrolysis process. This activation process aims to be able to open the pores of the catalyst surface and clean the catalyst from any impurities. The activation of the catalytic Cu is physically performed at a temperature of 300°C for 2 hours using the oven.

The Pyrolysis Process

The pyrolysis process began by mixing 250 grams of styrofoam waste with the activated Cu catalyst, which was then inserted into the reactor. Pyrolysis is performed at a temperature of 400°C with variations in the number of catalysts (0, 4, 6, 8, and 10%). The pyrolysis process is carried out by heating the reactor with a heater. Heated Styrofoam will melt and produce gas. The gas resulting from pyrolysis is flowed to the condenser circuit driven by cooling water so that the gas changes phase into liquid. The condensed liquid is collected in a measuring glass, and the volume is recorded every 10 minutes.

Kinetic analysis of reactions

The kinetic determination of reactions is carried out by calculating the activation energy value (Ea), the pre-exponential factor value (A), and the reaction rate constant (k) using the Arrhenius equation.

$$\boldsymbol{k = Ae^{\left(-\frac{Ea}{RT}\right)}} \qquad (1)$$

Where Ea is the activation energy (kJ/mol), T is the absolute temperature (K), R is the value of the constant gas (8.314 J/Kmol), and A is the pre-exponential factor value (minute-1).

The rate of change from solid to oil resulting from pyrolysis can be written as follows (Suwandono dan Hardianto 2019):

$$\boldsymbol{\frac{d\alpha}{dt} = kf(\alpha)} \qquad (2)$$

where α, t, k(T), f(α) is the degree of conversion of the process, time, constant reaction rate, and modeling of the reaction. In general, α is a form of oil addition resulting from pyrolysis and can be written as:

$$\boldsymbol{\frac{dv}{dt} = k.f\left(\frac{v - v\sim}{v^{\circ} - v\sim}\right)} \qquad (3)$$

Where Dv is the change in volume within a certain interval, Dt is the time interval for obtaining data, v is the volume at a certain time, vo is the initial volume, and v∼ is the final volume.

Basic equations for calculating kinetic parameters analytically.

$$\boldsymbol{k = \frac{A}{\beta} \, . e^{-Ea/RT}} \qquad (4)$$

Where B is the rate of heat.

The above equation is converted to logarithmic form due to the presence of an exponential equation. To eliminate the exponential value, all squares are multiplied by ln, thus becoming a straight-line equation to obtain the activation energy value and pre-exponential factor, where the plot for the x-axis is 1/T and for the y-axis is 1n k.

$$\boldsymbol{lnk = \frac{-Ea}{R}\frac{1}{T} + lnA} \qquad (5)$$

$$\boldsymbol{y = ax + c} \qquad (6)$$

Equations 5 and 6 are derivatives of equation 4 used to find the activation energy value (Ea) and the pre-exponential factor value (A). Once the activation energy value (Ea) is obtained, the pre-exponential factor value (A) is then used in equation 1 to find the reaction rate constant or reaction kinetics.

Result and Discussion

Effect of Cu catalyst on Pyrolysis Oil Volume

Based on the results of the study, the effect of the Cu catalyst on the volume of pyrolysis oil produced by styrofoam waste at a temperature of 400°C with a pyrolysis time of 70 minutes can be seen in Figure 1.

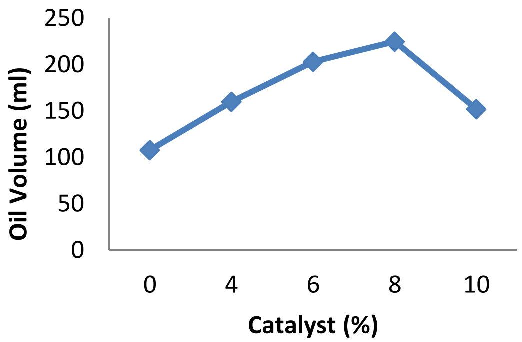

Figure 1: The Graphic Effect of the Cu Catalyst Pyrolysis Oil Volume

In Figure 1, it can be seen that the volume of oil resulting from pyrolysis tends to increase with the amount of catalyst used. This increase occurs because the catalyst will accelerate a reaction by lowering the energy of activation, or the minimum energy required for the reaction to occur in the process of breaking complex compound bonds into simpler ones (Salam dan Maryudi, 2018). This is in line with the research conducted by (Sadiya and Sri, 2015).

However, in Figure 1, it can be seen that there is a 10% decrease in the volume of oil resulting from pyrolysis in the catalysts. This is due to the large number of catalysts used in the pyrolysis process, which resulted in the formation of bulk between the styrofoam and the catalyst, thus making the catalytic function unoptimized, which makes the pyrolysis process not run effectively and causes a decrease in the volume of pyrolysis oil (Salam and Maryudi, 2018).

Asmara explains that the mechanism of the reaction of pyrolysis using the Zn catalyst, where the Zn catalyst is an acid catalyst so that the pyrolysis process can reduce the molecular weight of the polymer chain through a reaction with an acidic situation. The Zn catalyst causes the formation of carbonium ions and chain termination. Carbonium ions also play a role in the process of forming and breaking C-H bonds (Asmara and Kholidah, 2019). This is in line with the research carried out by Salamah, who conducted research by performing the pyrolysis process of styrofoam waste with Ni/silica catalysts (Salamah dan Maryudi, 2017).

According to Samara, the Zn catalyst is acidic. Similar to the Zn catalyst, the Cu catalyst is one of the acidic catalysts based on the Lewis theory, so the C-H dissociation reaction of the polystyrene molecule occurs. It causes the formation of carbonium and carbocation ions which cause the breaking of long polystyrene chains into simpler chains. This reaction causes the liquid product to increase and the formation of compounds.

Kinetic Analysis of Styrofoam Waste Pyrolysis Process Reactions with Cu Catalysts

Table 1: Produced oil volume and pyrolysis temperature in every 10 minutes

waktu (Menit)		Minyak Hasil Pirolisi (ml)								
		Katalis (%)								
	0	0	4	4	6	6	8	8	10	10
	Volume (ml)	Suhu (C)	Volume (ml)	Suhu (C)	Volume (ml)	Suhu (C)	Volume (ml)	Suhu (C)	Volume (ml)	Suhu (C)
10	0	99	0	97	0	98	0	96	0	98
20	0	155	0	148	0	130	0	143	0	148
30	0	183	0	178	0	172	6	194	0	183
40	8	210	10	206	40	200	78	248	8	206
50	38	279	42	289	147	270	144	305	69	270
60	79	350	110	352	190	358	206	360	108	352
70	108	400	160	400	203	400	225	400	152	400

In the reaction kinetics analysis of the pyrolysis process of styrofoam waste with Cu catalyst, it begins with calculating the value of the reaction rate constant (k) with equation 3, from the volume of oil produced at intervals of 10 minutes, as shown in the table above. After obtaining all the k values, it is necessary to find the value of ln k which is used to make a graph between ln k and 1/T where 1/T is obtained from the temperature in every 10-minute interval in kelvin units. From the ln k graph with 1/T, an equation will be obtained to find the value of the activation energy (Ea) and the pre-exponential factor (A). The ln k graph with 1/T for 0% catalyst can be seen in Figure 2.

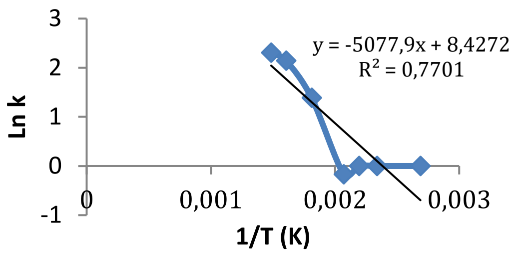

Figure 2. Graph ln k with 1/T for 0% catalyst

After obtaining the equation from the graph ln k with 1/T, in search for the activation energy value (Ea) with the equations 5 and 6, slope = -Ea/R, so obtain the Ea value of 42217.6606 kJ/mol. Meanwhile, to find the value of A with the equation ln C =ln B + intercept, B is the heating rate obtained from the temperature of the pyrolysis process for one hour for the 0% catalyst, which is 623 K or 10.383333 K/min. Then the result is inserted into the equation A = C/B so that the value of A is 4569.686677 minutes-1. After all the calculations of the activation energy values (Ea) and the pre-exponential factor (A) on all the catalyst variations used, the active energy value (EA) and pre-exponential factor (A) are obtained as shown in Figure 3 and 4,.

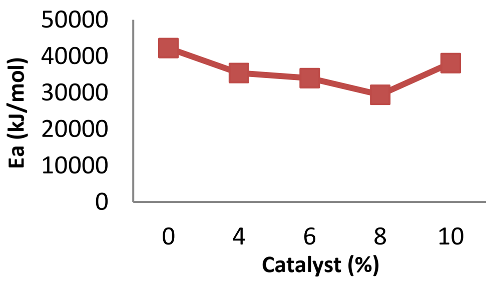

Figure 3. The graphic influence of the Cu catalyst on the Ea value

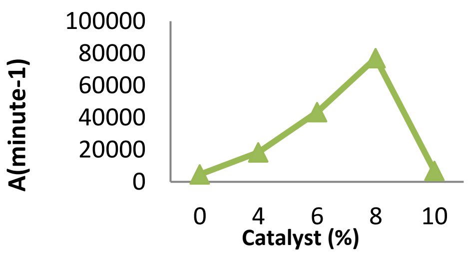

Figure 4. The Graphic Effect of the Cu Catalyst on A value

Based on Figure 3 and 4, it can be seen that the activation energy value (Ea) and the pre-exponential factor (A) decreased as the number of catalysts increased. The value of A increases with the increase in the number of catalysts. It is caused by the catalyst can lower the energy of activation, and the minimum energy required for a bond-breaking reaction to occur in a complex compound that becomes simpler (Yerimadesi, dkk, 2012).

From the values of Ea and A obtained, both are already in line with the theory of reaction kinetics. The faster the speed of the reaction, the lower the energy of activation, while the pre-exponential factor or collisions that occurs in the reaction will increase. This is in line with the research carried out by Purwani, who states that the faster the reaction takes place, the smaller the activation energy value (Ea) will be, and the value of the pre-exponential factor (A) will be greater because of the number of collisions that occur in the reaction (Purwani, Suyanti, dan Poernomo, 2016).

Once the Ea and A values are obtained for each catalyst, the value of the reaction rate constant or reaction kinetics values is calculated to see how fast the reaction takes place using the Arrhenius equation. The value of the reaction rate constant is shown in Figure 5.

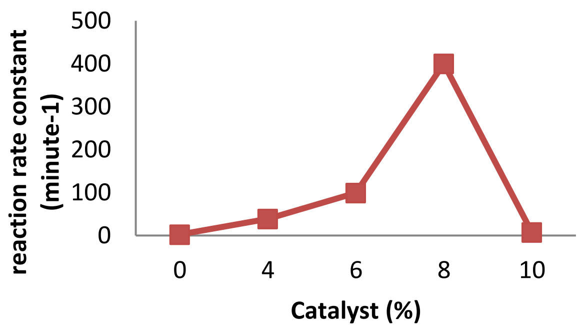

Figure 5. Graph of the relationship between reaction rate constants and the catalyst variation

On kinetic data, the results of the study of the pyrolysis process of styrofoam waste using the Cu catalyst show that the highest reaction rate constant (k) is the catalyst 8%, which is equal to 399.84 minutes-1. According to Wardana, since the catalyst is one of the factors affecting the reaction rate constant, one of its signs is that the pyrolysis time runs faster than the process without catalysts, and more results are obtained when using the catalyst (Wardana dan Veronika, 2015).

Based on the value of k obtained, it can be seen that an increase in the number of catalysts occurs, which indicates that the rate of reaction moves faster with the presence of the catalyst. This is following the research carried out by Irdiansyah, which states that the greater the value k, the faster the reaction rate will be, and the slower the reaction takes place, the smaller the value of k (Irdiansyah, 2017).

After analyzing all the reaction kinetics of the pyrolysis process of styrofoam waste using a Cu catalyst, it can be seen that the Cu catalyst accelerates the rate of reaction by lowering the activation energy and increasing the pre-exponential factor. This is following the statement delivered by Yerimadesi, stating that the catalyst accelerates the rate of reactions by lowering the energy of activation through the formation of substances between the reactions, and after the reaction is completed, the catalyst will return as it was, as well as increasing the intermolecular collision that makes reactions run faster (Yerimadesi, 2012).

Conclusion

Based on the results of the studies carried out, it can be concluded that the addition of Cu catalysts affects the reaction kinetics of the styrofoam waste pyrolysis process. The fastest reaction rate constant is 8% catalyst, while the slowest reaction rate constant is 0% catalyst. In a 10% catalyst, the reaction rate decreased, this was due to the formation of lumps between the catalyst and styrofoam which made the catalyst not work optimally.

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