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Thermal Cracking of Polyethylene Terepthalate (PET) Plastic Waste

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Abstract. In 2015, the United Nations Environment Program (UNEP) revealed that there are 280 million tons of plastic produced globally each year This research was conducted to convert plastic waste to be useful products. Polyethylene Terephthalate (PET) is converted into gas and coke using thermal cracking method and a stainless steel batch type reactor. Looking for the effect of temperature variations on the thermal cracking of PET plastic waste and studying the kinetic phenomena are the purpose of this research. A total of 40.17 grams of Polyethylene Terephthalate (PET) plastic waste was cracked in a batch reactor at 450, 500 and 550 ºC for 15, 30 and 45 minutes. The highest percent yield of gas (89.92%) was resulted at 30 minutes of reaction time and 550 ºC of the reaction temperature. The highest percent yield of coke (26.01%) was resulted at 45 minutes of reaction time and 500 ºC of the reaction temperature. The activation energy for the highest percent yield of coke, 26.01% is -9,257701 kJ/mol, otherwise the process needs to be revised to get the positive activation energy.

Keywords: polyethylene terephthalate (PET); catalyst; thermal cracking

1. Introduction

Energy conversion from waste materials such as plastic waste is increasingly being developed at this time. The types of plastic that are often used are PP (Polypropylene), PE (Polyethylene) and PET (Polyethylene Terephthalate).

The United Nations Environment Program (UNEP) revealed that losses from the disposal of plastic waste have reached USD13 billion, or as much as Rp. 153 trillion per year. In 2015, a study by UNEP and its partners estimated that 280 million tons of plastic were produced globally each year. Based on Indonesia is ranked second in the world as a producer of plastic waste to the sea which has reached 187.2 million tons after China which reached 262.9 million tons. Converting plastic waste into alternative fuel oil is one way to deal with plastic waste itself.[1]

In general, researches that have been done to convert plastic waste into energy are the research that wants to produce oil and gas fuel products, where fuel products can be form as hydrocarbons, such as gasoline or diesel and gas with an amount of C less than 5.[2-4]

Various attempts have been made to reduce the growth of plastic waste such as incineration and gasification processes. But, in these technologies, the process temperature is too high and the combustible gas is very dangerous. Finding other method to deal with the amount of plastic waste is a better way, one of that method is processing plastic waste to be alternative fuel by pyrolisis.[5-8]
Polystyrene and PET are types thermo-chemically treated plastic (as a recycling route) through pyrolysis in dynamic thermography. The behavior of the material is analyzed, especially the kinetics of the depolymerization reaction which is determined through general kinetics theory.[6-8]
Pyrolysis can have an important role for converting waste plastics into economically valuable hydrocarbons, which can be used either as fuel or feed stocks in the petrochemical industry.[9]
Thermally degradable polymers have been the center of thermal analysis studies for many years. Thermogravimetric analysis (TGA) is a general method for studying the degradation kinetics of polymers. Kinetic analysis is more effective for investigating the mechanism of degradation as a step in predicting the thermal stability of polymers.[10]
The activation energy of the degradation process is highly dependent on the polymerization method that determines the nature of the last group. The low activation energy can be related with impurity volatilization, (molecules with small volatility, catalyst residues, unreacted monomers).[11]
The rate law equation can be used to determine the price of k by drawing a graph In A versus t, then the gradient (slope) will be obtained by k and intersept of ln A.
For first order reaction :

$$\ln A = \ln A_o - k.t \quad (1)$$

The reaction rate constant (k) is not really constant, and the value is independent from the concentration of substances in the reaction. However, the reaction rate constant is very dependent on temperature until a scientist from Sweden named Arrhenius found the equation of the reaction rate constant (k) as a function of temperature.[10]

$$kA(T) = Ae\text{-}E/RT \quad (2)$$

Where, kA(T) the reaction rate constant of temperature T, A = frequency factor, e = natural number 2,71828, E = activation energy (kJ), R= ideal gas constant (8,314 J/mol K), T = absolute temperature (K).
Using stainless steel reactors with a batch system for thermal cracking, varying the temperatures and reaction times are expected to increase PET conversion.

2. Methodology

2.1. Instruments and materials

This research used cracking reactor from stainless steel. In addition, the equipment used in this research are included mortals, 100 mesh filters, digital scales, glassware, porcelain crushers, ovens, magnetic stirrers, Welch Duo Seal 1400 vacuum pumps, cylindrical furnaces. All of these tools are available at the Energy and Nano Materials Center, University of Jambi.
Polyethylene Terephthalate (PET) waste is obtained from the *Bank Sampah* Bangkitku, and then nitrogen gas and water.

2.2. Procedure

PET waste is washed and dried before sizing section by chopper machine. The sample needs to be cut into small pieces / chopped up to ± 2cm in size. Samples were put into the reactor with an initial mass of 40.17 grams. Batch reactor has function as a container where the cracking reaction takes place with the variations of temperatures as 450 ºC, 500 ºC and 550 ºC, and the cracking times as 15 minutes, 30 minutes and 45 minutes.

3. Results and discussions

3.1. Gas product

By comparing weight of gas with the initial sample weight, the percentation of gas can be obtained. Based on that comparison, at temperature 450 ºC, 500 ºC and 550 ºC, the highest yield of gas was obtained 89.82% where the time of thermal cracking was 30 minutes at temperature 550 ºC and the lowest yield of gas was obtained 73.99% where the time of thermal cracking was 45 minutes at temperature 500 ºC.

From this comparison, it can be made a graph of the relationship between the percentage of gas and cracking times.

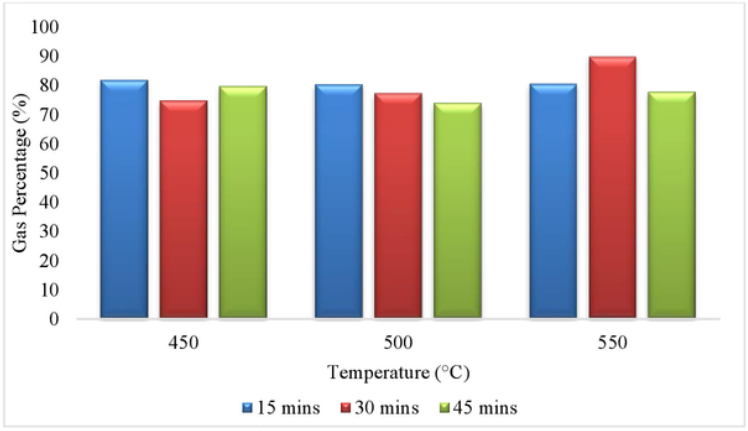

Figure 1. Comparison of gas percentage at varied temperatures and times

Figure 1 shows the comparison of gas percentage at varied temperatures and times, and then we can make a graphic for linear regression at varied temperatures and times in order to get K.

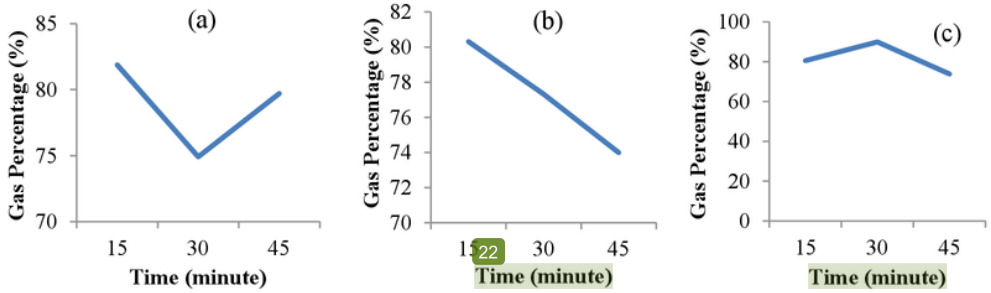

Figure 2. Graphic of gas product linear regression of K at (a) 450ºC, (b) 500ºC and (c) 550ºC

In figure 2a, the obtained R value was 0.5750 and the obtained K value was -0.07233. In figure 2b, the obtained R value was 5339 and the obtained K value was -0.2107. And In figure 2c, the obtained R value was 0.5339 and the obtained K value was -0.2107.

So that the equation obtained from the relationship between the gas percentage(%) with each cracking time:

$$[Y] = a + k_1x + k_2x^2 \quad (3)$$

Where, [Y] = gas percentage, a = intersept, k = slope (relationship between time and gas percentage, x = time (second).

3.2. Coke product

By comparing weight of coke with the initial sample weight, the percentation of coke can be obtained. Based on that comparison, at temperature at temperature 450ºC, 500ºC and 550ºC, the highest yield of coke was obtained 26.19% where the time of thermal cracking was 45 minutes at temperature 550ºC and the lowest yield of coke was obtained 10.16% where the time of thermal cracking was 30minutes at temperature 550 ºC.

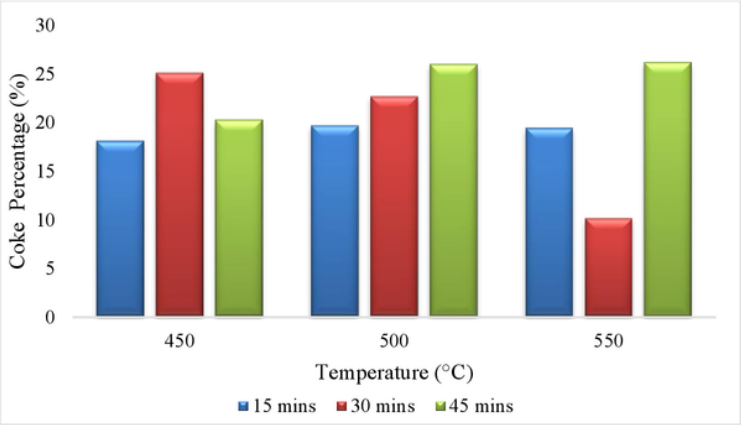

Figure 3. Comparison of coke percentage at varied temperatures and times

Figure 3 shows the comparison of coke percentage at varied temperatures and times, and then we can make a graphic for linear regression at varied temperatures and times in order to get K.

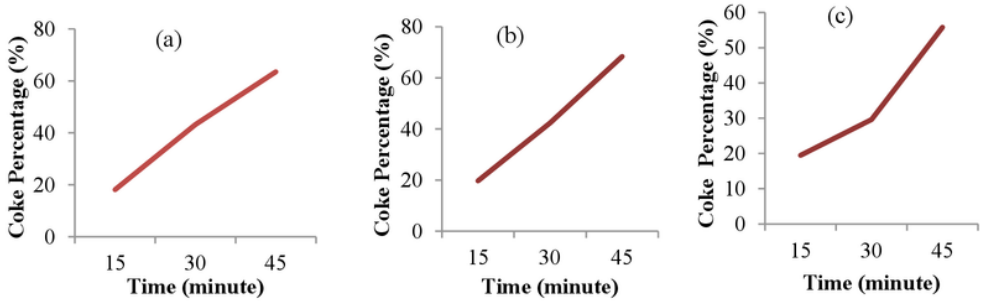

Figure 4. Graphic of coke product linear regression of K at (a) 450ºC, (b) 500ºC and (c) 550ºC

3.3. Kinetic analysis and determining activation energy for gas product

The exponential relationship between k and T from Arhenius equation can be seen in table 1. $k = k_0 - E/RT$, k_0 is frequency factor, E is activation energy, R is ideal gas constant, and T is absolute temperature.

Table 1. Relationship between 1/T versus ln k for gas product

T (ºC)	T (K)	1/T (K)	K	ln K
450	723	0,0014	-0,0523	-
500	773	0,0013	-0,0513	-
550	823	0,0012	-0,0548	-

E can be obtained from Arhenius equation where ln k = ln k0 – E/RT, with R is 8,314 J/mol K. However, ln K can not be obtained and neither slope, because K is negative. Activation energy for gas product in thermal cracking cannot be obtained because slope can not be determined.

3.4. Kinetic analysis and determining activation energy for coke product

The exponential relationship between k and T from Arhenius equation can be seen in table 2. k = k0 – E/RT, k0 is frequency factor, E is activation energy, R is ideal gas constant, and T is absolute temperature.

Table 2. Relationship between 1/T versus ln k for coke product

T (°C)	T (K)	1/T (K)	K	ln K
450	723	0,0014	1,4373	0,3627
500	773	0,0013	1,5188	0,4180
550	823	0,0012	1,1839	0,1688

E can be obtained from Arhenius equation, where ln k = ln k0 – E/RT and activation energy for coke is -9,257701 kJ/mol.K.

4. Conclusion

The highest yield of gas was obtained 89.82% where the time of thermal cracking was 30 minutes at 550°C . The lowest yield of gas was obtained 73.81% where the time of thermal cracking was 45 minutes at 550°C. And for coke, the highest yield of coke was obtained 26.01% where the time of thermal cracking was 45 minutes at 500°C . The lowest yield of coke was obtained 10.16% where the time of thermal cracking was 30 minutes at 550°C. Activation Energy from coke product in thermal cracking using stainless steel batch reactor is -9,257701 kJ/mol.K, it shows the process should be revised to get the positive activation energy and for gas product activation energy cannot be determined.

5. Acknowledgment

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