Kinetics Modeling of Waste Plastic Mixture Pyrolysis for Liquid Fuel Production

Govinda Aris Saputra, Chandra Wahyu Purnomo, PandjiPrawisudhaand, HarySulistyo

Abstract--- Plastic waste is very difficult to decompose completely since the process requires a long degradation time. One of the thermal treatment methods that can be used to reduce the amount of plastic wastein a relatively short of time is pyrolysis producing mostly liquid that can be used for fuels. Pyrolysis is a process of thermal degradation of polymeric materials such as plastics and organic materials such as biomass by heating without involving any oxygen molecules. The reaction mechanism that occurs in the pyrolysis process has not been observed properly. Most of the previous polypropylene pyrolysis research simplifies the reaction mechanism in which plastic decompose directly into three kinds of products causing some inaccuracy. This study aims to further investigated the reaction kinetics that occur in the polypropylene pyrolysis process. The pyrolysis process of polypropylene has been carried out with temperature variations of 350, 400, 450, 500 and 550 °C.The experimental data were fitted into the model equations and numerically adjusted to get the value of reaction rate constants. The calculation data is validated using the coefficient of determination to predict the right reaction mechanism. The results showed that by using the Kaufopanosreaction mechanism approach was well fitted with experimental data. The activation energy obtained using the model II mechanism is 201.51 kJ/mol.
Keywords: Pyrolysis, Polypropylene, kinetic, liquid fuel

I. INTRODUCTION

Plastic waste problem in Indonesia has entered a very worrying stage. It is estimated that more than 100 billion plastic bags are used by community every year and most of the plastic waste are not properly managed[1]. Plastic waste is very difficult to be decomposedcreating the accumulation in the environment. Debris created from plastic degradation called micro-plastics are also heavily polluting the water bodies.

Plastic is a synthetic organic material or semi-synthetic organic material. There are two plastic types i.e. thermoplastics and thermosetting polymer. Thermoplastic is a plastic that does not changes in chemical composition when it is heated and can be reformed.

Polyethylene, polystyrene, polyvinyl chloride and polytetrafluoroethylene (PTFE) are considered as thermoplastic. Meanwhile, thermosets can be melted and formed only once, so that after solidifiedit will remain solid.

Mostly, plastic based material comes from petroleum and natural gas. The plastic will break down when heated a few hundred degrees centigrade. Most of plastics are composed of polymers of carbon, and hydrogen with some oxygen, nitrogen, chlorine or sulfur[2].

Most of plastic waste now is only disposed in landfills ordirectly burned.The process has not solved all the problems of plastic waste, because the landfill process has not been able to decompose plastic waste. When it is burned at low temperatures, plastic waste will produceharmful compounds considered as carcinogens such as poly-chlorodibenzodioxin and poly-chlorodibenzofurans or simply called dioxins.

One method that can be used to reduce the amount of plastic waste while providing substitution for petroleum needs is pyrolysis. By using the concept, plastic waste is heated at a temperature of around 500°C converting solid phaseinto gaseous mixture, that can be further cracked. Then some part of gas can be condensed to becomes a liquid phasecan be used as a liquid fuel, while non-condensable gas can be used to heat up the equipment itself to create autothermal system.

There are four major variables determining the pyrolysis performance which are rate of heating, retention time, particle size, and temperature [3]. Temperature is correlate with how much the energy is supplied to the cracking system. It is expected that more gas and less liquid product will be obtained in a highly elevated temperature pyrolysis reactor.

Meanwhile there are several cracking mechanism of long chain plastic polymers such asrandom cutting polymer chains, and cutting the end of chain creating, which mechanism exist will be highly correlated with the covalent bond dissociation energy, degrees of aromatization as well as the presence of halogen and other heteroatoms in the polymer chain[4].

Previous finding reported that gradual increase of pyrolysis temperature will increase the volume of oil obtainedto a certain temperature level and then decrease [5]. For instance, in polyethylene pyrolysis with processing temperature of 400-500°C, it is found that the largest oil recovery occurs at a temperature of 450°C. The similar thing was shown by Undri et al.[6] there was a fluctuation in the amount of oil at a process temperature of 350-600°C, with the largest oil yield at a temperature of 400°C. Marcilla et al [7] explained that generally 500°C is a temperature that produces a maximum amount of liquid pyrolytic products.

It is necessary to further study the mchanism of reaction in order to scale up the system for larger capacity of plastic waste treatment. In this study pyrolysis process will be carried out using polypropylene raw materials with variations in temperature (350, 400, 450, 500, and 550 °C).

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Three reaction mechanisms will be compared and fitted to the experimental datas for finding the most suitable one.

II. EXPERIMENTAL

Material

The waste plastic used in this study is simplified to be represented by polypropylene (PP) plastic waste collected from a local recycle center as mineral water cups. Then the cup waste wassoaked in the water to clean it from the dirtprior to shredded into pieces (flakes) of about 0.5 to 1 cm in length. Then, the dried PP flakes was stored and ready to be pyrolyzed.

Pyrolysis Experimental

A simple pyrolysis set up has been prepared which consist of stainless-steel reactor with a programmable electric heater, condenser and a liquid-gas separator. Each of run, a 1000 g of polypropylene flakes was put into the reactor chamber and closed tight. Then, theheater raised the temperature up to the maximum temperature set upof 350, 400, 450, 500 or 550 °C.The maximum temperature was held constant until no liquid and gas product coming out from the phase separator. Liquid and gas product volume were measured every 10 minutes during each run. The char was also collected and weight after cooling down the reactor. The liquid product was characterized by Gas Chromatography and Mass Spectrophotometry QP2010S from SHIMADZU, while the high heating value was measured by a bomb calorimeter (Galenkamp).

Reaction Kinetic Models

A wide variety of kinetics models of pyrolysis reactions can be found in literature.In this study, three pyrolysis reaction models will be used to get the kinetic parameters.The first model, adopted from Shafizadeh dan Chin [8] and Thurner dan Mann [9], explains that in pyrolysis, material plastic (P) will simply break down directly into three yields i.e. gas (G), liquid (L), and solid or char (S) as shown in Fig 1. The equation (1) to (5) are derived from mass balance equation and will be used to determine the three rate constants (k1,k2 and k3).mP, mG, mC, mS, mM is the mass of plastic, gas, char and total solid remaining respectively at particular time (t).

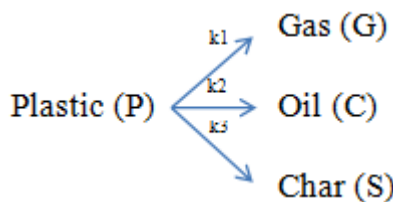**Fig 1. Reaction Mechanism in The First Model**

$$\frac{dmP}{dt} = -(k_1+k_2+k_3). \, mP \qquad 1$$

$$\frac{dmG}{dt} = k_1.mP \qquad 2$$

$$\frac{dmC}{dt} = k_2.mP \qquad 3$$

$$\frac{dmS}{dt} = k_3.mP \qquad 4$$

$$\frac{dmM}{dt} = \frac{dmP}{dt} + \frac{dmS}{dt} \qquad 5$$

Then, the second model of reaction mechanism assumes two stage of reactions as previously reported by Kaufopanos[10]. The first stage, plastic(P1) will form intermediate solid(P2) before decomposing into gas, liquid, and char as shown in Fig 2. The mass balance of this second reaction mechanism will derive a set of equation (Eq. 6-11), which is similar to the first order reaction with only addition of the mass of intermediate product (mP2) and one additional rate constant (k4).
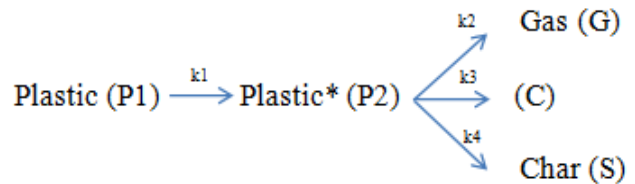

Fig 2. Reaction Mechanism in The Second Model

$$\frac{dmP1}{dt} = -k_1.mP1 \qquad 6$$

$$\frac{dmP2}{dt} = k_1.m.P1 - (k_2+k_3+k_4).mP2 \qquad 7$$

$$\frac{dmG}{dt} = k_2.mP2 \qquad 8$$

$$\frac{dmC}{dt} = k_3.mP2 \qquad 9$$

$$\frac{dmS}{dt} = k_4.mP2 \qquad 10$$

$$\frac{dmM}{dt} = \frac{dmP1}{dt} + \frac{dmP2}{dt} + \frac{dmS}{dt} \qquad 11$$

Meanwhile, the third model mechanism in Figure 3 shows that the raw plastic will decompose first into solids (S) and intermediate plastics (P2), from the intermediate the decomposed plastic becomes gas (G) and liquid (C)[11]. The char is produced in the first stage along with the intermediary plastic, while in the second stage the intermediate solid will further degraded into gas and liquid. Consequently, the mass balance will adapt to the third model and represented in equation 12 to 17.
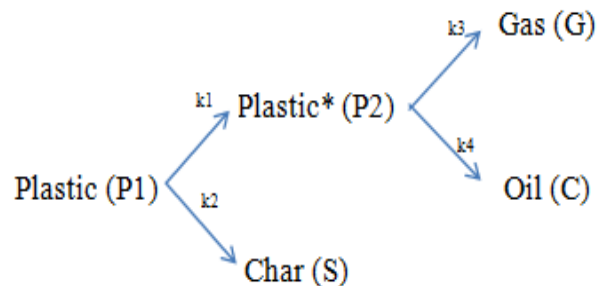

Fig 3. Reaction Mechanism of The Third Model

$$\frac{dmP1}{dt}= -(k_1+k_2).mP_1 \qquad 12$$

$$\frac{dmP2}{dt}= k_1.mP_1-(k_3+k_4).mP_2 \qquad 13$$

$$\frac{dmC}{dt}= k_4.mP_2 \qquad 14$$

$$\frac{dmG}{dt}= k_3.mP_2 \qquad 15$$

$$\frac{dmS}{dt}= k_2.mP_1 \qquad 16$$

$$\frac{dmM}{dt}= \frac{dmP1}{dt} + \frac{dmP2}{dt} + \frac{dmS}{dt} \qquad 17$$

Arrhenius equation was used to calculate the activation energy with the reaction rate constant obtained from the above mass balance equations.

Result and Discussion

Effect of Temperature on Pyrolysis Product Yield

Temperature provides energy for polypropylene plastic decomposition process. The distribution of product yield among liquid (oil), gas, and solidswill be heavily affected by the reaction temperature. Distribution of product yield on various temperatures is provided in Table 1. Based on Table 1, the results of study show that smallest solid yield was obtained at 550 °C with the value of 0.81% and largest solid yield at 350°C (34.95%). Higher temperature causes more compounds can beevaporated. These vaporized compounds will be transformed to oil and gas product by partial condensation.

The yield of polypropylene pyrolysis oil has increased with increasing pyrolysis temperature. This is because the temperature influences the rate of decomposition reactions. At higher temperature, the possibility of decomposition reactions is higher that will lead to shorter chain product in the form of liquid or gas. However, at the highest 550°C there is a decrease in pyrolysis oil yield. This could be due to a further chain cracking reaction of the polymer bond producing smaller gaseous particles which is difficult to be condensed (non-condensable gas).

Table1 Yield with Variation Temperature

Temp (°C)	Yield Char	Yield Oil	Yield Gas
350	0.3495	0.44	0.21
400	0.0113	0.78	0.21
450	0.0106	0.80	0.19
500	0.0104	0.81	0.18
550	0.0081	0.78	0.21

Since the vapor flow is rely on the natural driving force only, it should be noted that at higher temperatures the plastic vapor is traveling faster inside the reactor chamber due to its higher kinetics effect and larger density difference. This will lead to shorter reaction time and reduce the possibility of long chain molecule to be cracked. This could be the reason why at 550 °C there is a reduction in gas yield. On the other word, at higher temperature the reaction rate is faster but shorter residence time that may lead to reduction of the gaseous product.
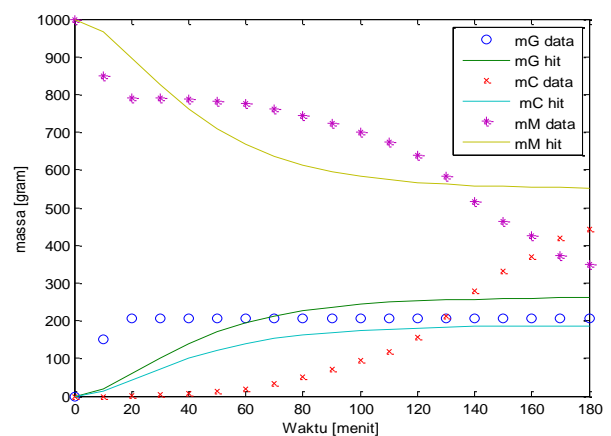
Kinetic modeling

In this study, several reaction kinetics models are applied to understand the reaction mechanism. During the pyrolysis experiment, the data that can be obtained arethe mass of liquid product and mass of the generated gas with respect to time. Meanwhile the mass of solids can only be measured before and after the process.

The reaction mechanism of the model is fitted with experimental data in the temperature range of 350-550 °C. Evaluation of the reaction constants was done using Matlab simulation program. An example of curve fitting data was represented in Figure 4, while the reaction rate constants are listed in Table 2.

Figure 4 shows data fitting of gas, liquid and solids mass with respect to time between experimental data and calculation of models at some temperature. Simulation data will calculateeach reaction rate values. Connecting ln k with (-1/T) the value of Ea and A0 can be determined and listed in Table 2.

Meanwhile, activation energy which represents the amount of energy requirement for a reaction to occur has been listed in Table 2 for each of reaction set in each model. It is shown that the first model has comparable initial energy for each product. Meanwhile for the second and third model the highest activation energy is for the first stage of reaction which is transformation of plastic into intermediate product. This finding is reasonable since the gas and liquid products were obtained at an elevated temperature during experiment. Thus, the supply of heat at the initial stage of heat treatment is used for changing the plastic into intermediate product before proceed to the final products of gas and liquid.
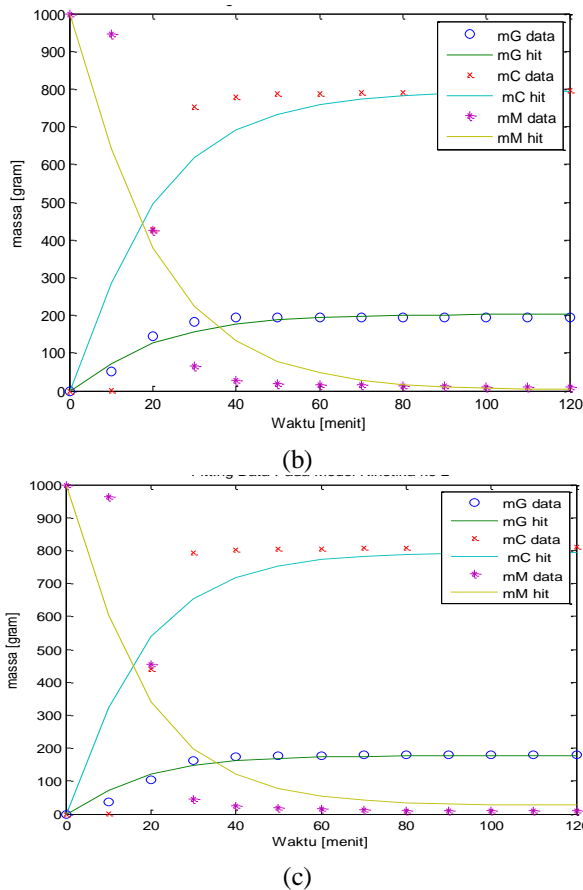

(a)

(b)

(c)

Fig 4.Data Fitting of Second Reaction Mechanism (a) 350 °C, (b) 450 °C, and (c) 500 °C

To evaluate the best fitted proposed model, R-Square method is used and presented in Table 3. The R square is calculated for both reaction in gas phase and liquid phase (oil). At the lowest heat treatmenttemperature, it is shown that all the models cannot fit the data very well. It could be due to unstable pyrolysis reaction at low temperature. Meanwhile, other than the lowest temperature mostly the models can closely approach the experimental data. For gas phase, it can be observed that the second reaction model has higher R-Square values compared with the other. It is also applied for the oil phase that suggest the second model to be the best reaction mechanism based on the data obtained.

The pyrolysis of polypropylene used heating rate of 10°C /min that can be categorized as slow pyrolysis. In the early stage of slow pyrolysis,it is observed that a large amount of smoke or non-condensable gas is produced. After the temperature passes 250°C the oil dropletsstarts to appear after passing through the condenser.

Table2 Parameter of Pyrolysis Reaction Kinetic

Model	Arrhenius equations	Ea (kJ/mol)
I	$k_1= 36.014\exp -\frac{45.27}{RT}$	45.27
	$k_2=19,912.44\exp -\frac{76.86}{RT}$	76.86
	$k_3= 12.68\exp -\frac{40.92}{RT}$	40.92
II	$k_1= 260,146.44 \exp -\frac{82.42}{RT}$	82.42
	$k_2=11.78\exp -\frac{38.97}{RT}$	38.97
	$k_3= 7.2 \exp -\frac{31.88}{RT}$	31.88

	$k_4= 2.82 \exp -\frac{48.24}{RT}$	48.24
III	$k_1= 260,146.44 \exp -\frac{70.51}{RT}$	70.51
	$k_2=11.78\exp -\frac{15.97}{RT}$	15.97
	$k_3= 7.2 \exp -\frac{8.78}{RT}$	8.78
	$k_4= 2.82 \exp -\frac{40.57}{RT}$	40.57

This observation has good correlation with the second reaction model. PP plastic raw materials will be transformed into plastic intermediates first during early heat treatment dominated by mostly volatile matter vaporation. Then, cracking process starts from plastic intermediate into pyrolysis products, namely gas, liquid (oil) and solids (char) will be proceed at the higher temperature to the end of process. So it can be concluded that model II can represent mechanism that occurs in the process of pyrolysis of polypropylene.

Tabel 3 The results of the R-Square value on model I, II and III for the results of gas and oil

R-Square						
Temp (°C)	Model I		Model II		Model III	
	Gas	Oil	Gas	Oil	Gas	Oil
350	0,33	0,71	0,43	0,45	0,42	0,57
400	0,86	0,60	0,97	0,97	0,89	0,63
450	0,75	0,57	0,96	0,91	0,85	0,85
500	0,61	0,50	0,96	0,90	0,94	0,87
550	0,74	0,59	0,95	0,85	0,90	0,77

For model I it is not suitable to be used in this mechanism since it is more suitable for fast pyrolysis. In a fast pyrolysis it uses a high heating rate and fast residence time so that the plastic raw material will decompose rapidly into gas, liquid (oil), and solid (char). Meanwhile, model III has similarity with model II since it composes by two stage reaction. However, it is quite unrealistic if the char is formed in the early stage.

Calculated from Table 2, the total activation energies in models I, II and III are 163.05 kJ / mol, 201.51 kJ / mol and 135.83 kJ / mol. Aboulkas et al., [8]conducted pyrolysis using various types of plastic and reported that activation energy for High Density Poly Ethylene plastics was 238-247 kJ / mol, Low Density Poly Ethylene plastics was 215-225 kJ / mol and Polypropylene was 184-218 kJ / mol. Another researcher also found a similar range of activation energy of Polypropylene pyrolysis at about 192 – 237 kJ/mol[9].

CONCLUSION

PP pyrolysis for optimizing the liquid product for fuel can be obtained at temperature of 500°C. The most suitable reaction mechanism is represented by model II, which predict the existence of intermediary product of plastic before transforming into final product of gas, liquid and remaining char.

REFERENCES

1. Purwaningrum (2016) "Upaya Mengurangi Timbulan Sampah Plastik," Jurnal Teknik Lingkungan, 8(2), hal. 141–147.
2. Caglar, A. dan Aydinli, B. (2009) "Pyrolysis Isothermal Co – Pyrolysis of Hazelnut Shell and Ultra High Molecular Weight Polyethylene : The Effect of Temperature and Composition on the Amount of Pyrolysis Products," Journal of Analytical and Applied, 86, hal. 304–309.
3. Basu, P. (2010) "Biomass Gasification and Pyrolysis: Practical Design and Theory," in Academic Press. Elsevier.
4. Xingzhong, Y. (2006) "Converting Waste Plastics into Liquid Fuel by Pyrolysis: Developments in China," in Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels. Chichester: John Wiley &Sons, Ltd, hal. 729–750.
5. Dewi, I. N. D. . (2014) Karakteristik Minyak Hasil Pirolisis Batch Sampah Plastik Polyethylene dan Polystyrene pada Berbagai Suhu. Universitas Gadjah Mada.
6. Undri, A., Rosi, L. dan Frediani, M. (2014) "Fuel From Microwave Assisted Pyrolysis Of Waste Multilayer Packaging Beverage," Journal Of Fuel, 133, hal. 7–16.
7. Marcilla, A., Beltrán, M. I. dan Navarro, R. (2009) "Evolution of products during the degradation of polyethylene in a batch reactor," Journal of Analytical and Applied Pyrolysis, 86(1), hal. 14–21. doi: 10.1016/j.jaap.2009.03.004.
8. Shafizadeh, F. dan Chin, P. P. S. (1977) "Thermal Deterioration of Wood," ACS Symposium Series, 43, hal. 57–81.
9. Thurner, F. dan Mann, U. (1981) "Kinetic investigation of wood pyrolysis," Industrial & Engineering Chemistry Process Design and Development, 20(3), hal. 482–488. doi: 10.1021/i200014a015.
10. Koufopanos, C. A., Maschio, G. dan Lucchesi, A. (1989) "Kinetic Modelling of the Pyrolysis of Biomass and Biomass Components," The Canadian Journal of Chemical Engineering, 67, hal. 75–84.
11. Yuniarti (2016) Tinjauan Kinetika Reaksi Pirolisis Cangkang Biji Ketapang Untuk Menghasilkan Bahan Bakar Briket Arang. Universitas Gadjah Mada.
12. Aboulkas et al., (2011) "Bioresource Technology Pyrolysis of olive residue and sugar cane bagasse : Non-isothermal thermogravimetric kinetic analysis," Bioresource Technology. Elsevier Ltd, 102(24), hal. 11234–11238. doi: 10.1016/j.biortech.2011.09.010.
13. Westerhout, R. W. J. et al. (1997) "Kinetics of the Low-Temperature Pyrolysis of Polyethene , Polypropene , and Polystyrene Modeling , Experimental Determination , and Comparison with Literature Models and Data," (1), hal. 1955–1964.