Kinetic study on the pyrolysis of low-density polyethylene (LDPE) waste using kaolin as catalyst

Emi Erawati, Hamid, Danik Martenda

Chemical Engineering Department, Engineering Faculty, Universitas Muhammadiyah Surakarta, Jl. A. Yani Tromol Pos I, Pabelan, Kartasura, Surakarta 57102, Indonesia

email: emi.earawati@ums.ac.id

Abstract. The increase in the industrial and urban activities has resulted in the rise of plastic production and consumption. The higher demand for plastic causes accumulation of plastic waste in which it contributes to environmental problems. About 65-70% of plastic waste is a type of Low-Density Polyethylene (LDPE). To reduce this type of waste, the pyrolysis method can be an alternative. This study investigated the catalyst ratio and particle size of the material. The results indicate that the optimum catalyst was at 15% wt/wt with liquid and gas yields of 99.15% and 0.85%, respectively. Meanwhile, the optimum particle size variation is at 7.5 x 6.5 cm with liquid and gas yields of 99.82% and gas 0.18%, respectively. The proximate analysis of LDPE wastes includes the analysis of ash content, volatile matter, and fixed carbon, with the values of 0.35, 99.61 and 0.04% wt/wt, respectively. The chemical composition is analyzed using Shimadzu GCMS-QP2010S. The highest percentage component is heptane. The fuel analysis shows pyrolysis oil products comply with the national standard set by the regulation No. 14499 KJ14/DJM/2008. The reaction kinetics of the liquid and gas activation energy are of 127,025.79 J/mol and 73,766.93 J/mol, respectively. Meanwhile, the liquid and gas pre-exponential factors are 8,590 and 257, respectively.

1. Introduction

Global demand for plastic has increased significantly due to the rapid population growth. It is the result of the application of plastic that dominates various sectors, including construction, packaging, electronic, and automotive. The global production of plastic increased from 322 million tons in 2015 into 348 million tons in 2017 [1]. The increasing demand for plastic inevitably causes the accumulation of plastic waste that contributes to serious environmental problems. Plastics, also called polymers, cannot be decomposed and produced through a polymerization process. They are produced from petroleum derivatives, especially carbon and hydrogen plus additives [2]. Polyethylene (PE) has been reported to have a carbon content ranging between 83.9 and 86.1%, while polypropylene (PP) has a range of carbon between 85.5 and 86.1% [3][4][5]. About 65-70% of plastic waste is made from LDPE, HDPE, and PP [6], while about 17.5% is plastic made from LDPE. This research specifically discusses LDPE plastic waste. LDPE are usually used as material for plastics for packaging, food wrapping, and flexible water bottles [7].

The high amount of LDPE wastes has urged the search for suitable and environmentally friendly methods for waste management. Currently, such wastes are disposed through land filling method. The other waste treatments include incineration and recycling. However, land filling method does not solve
the problem because it requires a large area and does not involve decomposition process hence it is considered less effective [8]. Meanwhile, the incineration method can stimulate the greenhouse effect such as chlorofluorocarbons (CFC), dinitrogen monoxide (N₂O), methane (CH₄), and carbon dioxide (CO₂) [9].

The recycling method can be an option to reduce the amount of plastic waste, but more reliable and sustainable alternatives are still needed. Moreover, high demand of plastics is increasing every year, while the availability of fossil fuels such as coal, gas and especially petroleum as the material of plastic is declining. Therefore, many researchers are interested to discover and develop potential energy resources due to the rise of energy demand. One of methods that is claimed to be safe and environmentally friendly is pyrolysis, which is a process of thermal degradation of long chain polymers into shorter chains by heating them in the absence of oxygen. The process generates three major products, namely oil, gas, and char, which are useful for industries and refineries. Pyrolysis has been extensively implemented because this process is able to produce oil products up to 80%wt at a moderate temperatures of 500 °C [10]. Furthermore, pyrolysis has several advantages, including very flexible, thus the materials can be manipulated to gain the optimum liquid oil yield. The product can be used as fuel for furnaces, boilers, turbines, and diesel engines, without any necessity to perform other treatments [11]. However, pyrolysis process requires a catalyst, among other is kaolin. It is expected that by using kaolin as the catalyst, the pyrolysis reaction will be faster and more effective.

The aims of the present study are to carry out a proximate analysis on the characteristics of raw material, investigate the influence of the ratio of raw material to catalyst as well as surface area to liquid and gas yields, determine the activation energy and pre-exponential factor, and examine fuel specification based on Indonesian regulation.

2. Raw Materials and Methods

2.1. Raw Materials

The raw material used in the pyrolysis process was clear colored plastic bag waste while white kaolin powder was used as the catalyst. The proximate analysis of LDPE was carried out. The parameters are presented in Table 1.

| Parameters       | (% wt/wt) |
|------------------|-----------|
| Ash contents     | 0.35      |
| Volatile matter  | 99.61     |
| Fixed carbon     | 0.04      |

Proximate analysis is used to measure the chemicals properties of the plastic compound based on several parameters, i.e., ash content, volatile matter, and fixed carbon [12]. Ash content and volatility matter have been identified as the major factors that influence the yield of liquid oil from the pyrolysis process. High volatile level will produce high liquid oil yield, while high ash content will reduce the yield of liquid oil hence it can increase the yields of gas and char [13]. Based on the result of proximate analysis, LDPE plastics produce a high level of volatile matter while the ash content is relatively low. This result shows that LDPE plastics relatively produce high liquid yields.

2.2. Experiment

The pyrolysis equipment consists of a single reactor with a diameter of 20 cm and a height of 30 cm, a series condenser, a thermocouple, three liquid storages, a manometer, and three gas storages. The LDPE plastic wastes were cleaned and then accurately weighed. Single samples were 500 grams in weight. As the catalyst, kaolin was prepared with four weight variations of 5, 10, 15, and 20 wt/wt %. Subsequently, 500 grams of raw materials with various weight variations of catalyst were inserted into the reactor. Further step was to turn on the cooling water pump (aerator), the reactor heater, and the thermocouple for 100 min and yield retrieval was carried out every 20 min. The liquid yields were
stored in the 250 mL erlenmeyer flasks. The volume and weight of the yield of liquid product were measured on the digital balance to determine the mass of liquid retrieved every 20 minutes. The volume of gas and the pressure changes on the manometer were also measured every 20 minutes. After 100 minutes, the pyrolysis process was discontinued by turning off the electricity and liquid petroleum gas flow. The reactor was opened when the reactor temperature was normal in order to avoid any remaining volatile matter of during the cold decomposition process. The pyrolysis process was repeated on the variations of surface area.

2.3. The effect of catalyst weight variation and surface area on the mass of liquid and gas yield

Figures 1 and 2 show the change in the mass of liquid and gas pyrolysis products of LDPE plastics of the control and various weight variations of catalysts of 5, 10, 15, and 20% wt/wt. Furthermore, Figure 3 and 4 show the change in the mass of liquid and gas pyrolysis product of LDPE and the mass of the products on the various surface areas, namely variation I (17.5 x 15 cm), variation II (7.5 x 13 cm), and variation III (7.5 x 6.5 cm).

In the pyrolysis process, catalyst has the function of reducing the activation energy so as to increase the reaction rate. Figure 1 shows the performance of the catalyst requires the optimum temperature. There is a significant difference between the pyrolysis process using catalysts compared to the control in which the pyrolysis process of the control generates higher amount of liquid yield produced from every product retrieval than those generated from the pyrolysis process using catalyst.

Furthermore, Figure 2 illustrates the changes in the mass of gas products. The mass of the gas mass is influenced by several parameters such as temperature, heating rate, pressure, and residence time.
According to Basu [15], the conditions that strongly support the formation of gas are high temperature and long residence time. Onwudili [16] also proves that the higher the pyrolysis temperature is, the lower the yield of liquid oil while the higher the yield of gas. Based on Figure 2, the highest mass of gas is produced by a catalyst with weight variation of 10% wt/wt while the lowest is produced by a catalyst of 15% wt/wt.

Figures 3 and 4 show the change in the mass of liquid and gas products based on the variations of surface area. In general, smaller particles will have larger surface area to accelerate the reaction process. Therefore, the smaller the particle size, the higher the mass of liquid product [17].

Figure 5 and Figure 6 illustrate the relationship between the weight variations of catalyst and the variations of surface area to the liquid and gas yields. Figure 5 indicates that the catalyst of 15% wt/wt produced the highest liquid and the lowest gas yield of 99.15% and 0.85%, respectively. Meanwhile, the control and the weight variations of catalyst of 5 and 20% wt/wt generate a relatively similar liquid product of 90%. It is interesting to note that the variation of catalyst of 10% wt/wt produces the lowest liquid yield. It is an evidence that the higher ratio catalyst to raw material does not generate optimum liquid yield. It is because the high ratio or excess catalyst will increase the yield of the gas and decrease the liquid yield at the same time. Figure 6 describes the relationship between the variation of surface area and the liquid and gas yields. It is noticeable that the pyrolysis process in the variation II and III only produces liquid yield but not gas product. The highest liquid yield is produced by the smallest surface area variation. The optimum liquid yield and gas yield produced by the smallest surface area are 99.78% and 0.22%, respectively.

![Figure 5](image1.jpg)  
**Figure 5.** Relationship between liquid and gas yield (%) to catalyst variations

![Figure 6](image2.jpg)  
**Figure 6.** Relationship between liquid and gas yield (%) to surface area variations

2.4. Relationship between temperature and time on the weight variation of catalyst and the variation of surface area

Figure 7 and 8 show the changes in temperature and time on the variation of catalyst and surface area.
The results show that longer pyrolysis process will result on higher temperature. The pyrolysis temperature will rise until the optimum temperature and then it will tend to decline. The optimum temperature for product yield is different in which as the raw material, LDPE plastics have an optimum temperature of about 450°C. Figure 7 shows the pyrolysis process using a catalyst of 15% is able to reach the optimum temperature and produce higher liquid yield. The equation for the relationship between temperature and pyrolysis time on the variation of catalyst is presented in Table 2 while on the variation of surface area in Table 3.

### Table 2. Equation of the relationship between equation and time on catalyst variation

| Catalyst Variation (wt/wt%) | Equation for Temperature |
|-----------------------------|--------------------------|
| Control                     | $T = 3.23t + 171.67$     |
| 5 wt%                       | $T = 3.7086t + 145.9$    |
| 10 wt%                      | $T = 2.7343t + 190.29$   |
| 15 wt%                      | $T = 3.4757t + 194.05$   |
| 20 wt%                      | $T = 3.6929t + 117.52$   |

### Table 3. The equation of temperature and time on surface area variation

| Surface Area Variation      | Equation for Temperature |
|-----------------------------|--------------------------|
| Variation I                 | $T = 3.5343t + 176.29$   |
| Variation II                | $T = 3.5443t + 202.95$   |
| Variation III               | $T = 3.1071t + 199.14$   |

#### 2.5. Fuel Properties of the Pyrolysis of LDPE Plastics

The result of the analysis of liquid oil products is presented in Table 4. The purpose of testing the pyrolysis result is to determine the oil products is compliant with the standards set on the decree of the Director General of Oil and Gas, Ministry of Energy and Mineral Resources of the Republic of Indonesia, No. 14499.K/14/DJM/2008 on the standards and quality (specification) of fuel marketed in Indonesia. The specific gravity of LDPE is 0.7901 g/cm³. This value is comparable to the standard specific gravity of fuel diesel. API gravity is the method developed by the American Petroleum Institute (API) used for measuring the density of petroleum relative to that of water [18]. Nevertheless, the API gravity of LDPE plastics is 46.7, which is not comparable to the commercial diesel fuel. The gross heating value (GHV) also known as calorific value is an important parameter to measure fuel characteristics. The calorific value of a fuel is the energy produced when the fuel is completely burned in sufficient air [19]. The calorific value of LDPE oil is 46.4186 MJ/kg, the value is higher than the SNI standard in which the higher value of GHV indicates the better quality of fuel oil. Flash point is the
lowest temperature of the fuel to vaporize and mix with air so that it will ignite instantly when passes the test frame under certain conditions [20]. The flash point of LDPE pyrolysis oil is less than 25°C, which is below the standard. It shows that the pyrolysis oil is very flammable. Pour point is defined as the temperature at which the fuel stops to flow [21]. Generally, the increased viscosity of the liquid can reduce the flow of liquid. The pour point value of LDPE is 12°C, meaning that LDPE oil cannot flow at temperatures below 12°C. Viscosity is defined as a measure of a fluid’s resistance to flow [22].

| Physical properties                  | Unit      | SNI          | LDPE     |
|--------------------------------------|-----------|--------------|----------|
| Specific gravity at 60/60°C          | g/cm³     | 0.742        | 0.7901   |
| API gravity                          | -         | 30-42        | 46.7     |
| Gross Heating Value                  | MJ/kg     | >41.87       | 46.4186  |
| PMCC Flash Point                     | °C        | Min 60       | <25      |
| Pour Point                           | °C        | Max 18       | 12       |
| Kinematic viscosity at 40°C          | mm²/s     | 2.0-5.0      | 2.199    |

### Chemical properties of LDPE pyrolysis oil

Figure 9 describes the chromatogram of LDPE waste plastic. The analysis of chemical composition of the oil shows there are 67 chemicals in which the highest percentages include heptane, hexane, octane, nonane, and 1-octene. Table 5 shows the main chemical compounds from LDPE pyrolysis oil.

![Figure 9. LDPE pyrolysis oil chromatogram](image)

| Area (%) | Compound | Name       |
|----------|----------|------------|
| 7.31     | C₇H₁₆    | Heptane    |
| 7.00     | C₆H₁₄    | Hexane     |
| 6.07     | C₆H₁₈    | Octane     |
| 4.15     | C₈H₂₀    | Nonane     |
| 3.69     | C₆H₁₆    | 1-Octene   |

### Pyrolysis kinetics reaction of LDPE waste

The determination of pyrolysis kinetics reaction of LDPE waste has been done using mechanism model developed by Koufopanosi. This model is divided into two models. The first model produces intermediate products and later will become gas and char products after the degradation process, while the second model produces three pyrolysis products, namely liquid, gas, and char. Both models are shown in Figure 10 and 11. Meanwhile, in this study, the second mechanism model is modified as shown in Figure 12.
Figure 10. First model of Koufopanosi’s Mechanism

Figure 11. Second model of Koufopanosi’s Mechanism

The kinetics equation of each component is expressed in the following equations of (1), (2) and (3).

\[ \frac{dP}{dt} = -k_1 P - k_2 P \]  
\[ \frac{dC}{dt} = k_1 P \]  
\[ \frac{dG}{dt} = k_2 P \]  

The determination of the rate constant of the reaction using the Arrhenius equation is expressed in the equation (4) as follows:

\[ k = A \exp\left(-\frac{E}{RT}\right) \]  

where \( T = f(t) \) empirical

In the modification of the second model of Koufopanosi’s mechanism model, LDPE waste will degrade into liquid and gas products. To determine the value of the activation energy (\( E \)) and pre-exponential factor (\( A \)), programming software is used. Table 6 shows the value of activation energy (\( E \)), pre-exponential factor (\( A \)), and Sum Square Error (SSE) in the weight variation of catalyst and the surface area variations.

| Variables              | \( E_1 \), J/mol | \( E_2 \), J/mol | \( A_1 \)       | \( A_2 \)       | SSE     |
|------------------------|------------------|------------------|-----------------|-----------------|---------|
| Catalyst variation     | 237,396.92       | 119,037.88       | 2.20 \times 10^{14} | 1.51 \times 10^6 | 220.24  |
| Surface area variation | 127,025.79       | 73,766.93        | 8,590           | 257             | 36.18   |

The changes in the mass of liquid and gas between research and processing data in the percentage of catalyst and surface area variation are provided in Figure 13 and Figure 14.
Figure 13. The simulation of the results in catalyst variation, (a) control, (b) 5% wt/wt, (c) 10% wt/wt, (d) 15% wt/wt, and (e) 20% wt/wt.
The kinetics parameters with low density polyethylene (LDPE) as the raw material have been investigated prior to the present study. The comparison is presented in Table 7.

Table 7. Comparison of kinetics parameters for LDPE

| Raw Material                          | E₁, J/mol | E₂, J/mol | A₁        | A₂        | Reference |
|---------------------------------------|-----------|-----------|-----------|-----------|-----------|
| LDPE plastic bag (black colour)       | 251,000   | 244,000   | 2.45x10¹⁷ | 5.6x10¹⁶  | [23]      |
| LDPE plastic waste                    | 194,000   | -         | 1.4x10¹³  | -         | [24]      |
| Commercials plastic                   | 220,500   | -         | 3.66x10¹⁹ | -         | [4]       |
| Clean non-coloured samples of LDPE    | 340,800   | -         | 9.55x10²¹ | -         | [3]       |
| LDPE waste samples                    | 333,430   | -         | 6.52x10²¹ | -         | [25]      |

3. Conclusion
The pyrolysis process of LDPE waste has been done and it shows the optimum yield of liquid and gas products are generated by the catalyst variation of 15% wt/wt, of 99.15% and 0.85%, respectively. From GCMS, heptane is the highest chemical as the result of liquid product. The reaction kinetics parameters of the liquid and gas activation energy are 127,025.79 J/mol and 73,766.93 J/mol, respectively. Meanwhile, the liquid and gas pre-exponential factor are 8,590 and 257, respectively.

4. Acknowledgements
The authors would like to express their utmost gratitude for the financial sponsorship from the Ministry of Research, Technology, and Higher Education of the Republic Indonesia through the Penelitian Strategis Nasional Institusi Scheme, Contract Number: 72.61/A.3-III/LPPM/III/2018.

References
[1] Association of Plastics Manufacturers 2018 An analysis of European plastics Production, Demand and Waste Data The European Association of Plastics Recycling and Recovery Organisations Belgium 1–60, 2018.
[2] Olufemi A S and Olagboye S A 2017 Thermal Conversion of Waste Plastics into Fuel Oil Int J Petrochem Sci Eng 2 1–7
[3] L. Sorum M. G. Gronli and J E Hustad 2001 Pyrolysis characteristics and kinetics of municipal solid wastes Fuel 80 1217–1227
[4] Encinar J M and González J F 2008 Pyrolysis of synthetic polymers and plastic wastes. Kinetic study Fuel Processing Technology 89 678–686
[5] Al-salem S M, Antelava A, Constantinou A, Manos G and Dutta A 2017 A review on thermal and catalytic pyrolysis of plastic solid waste (PSW) Journal of Environmental Management
197 177–198
[6] Sonawane Y B, Shindikar M R and Khaladkar M Y 2016 Transforming Low Density Polyethylene Waste into Diesel Grade Fuel by Catalytic Pyrolysis Int. J. Res. Chem. Environ 6 10–15
[7] R P Liestonio M S Cahyono W Widyawidura A Prasetya and M Syamsiroy 2017 Karakteristik Minyak dan Gas Hasil Proses Dekomposisi Termal Plastik Jenis Low Density Polyethylene (LDPE) Jurnal Offshore 1 1–9
[8] Ermawati R 2011 Converting of plastic waste as a source of energy alternative Jurnal Riset Industri 5 257–263
[9] Kyaw K T and C S S Hmwe C S C 2015 Effect Of Various Catalysts On Fuel Oil Pyrolysis Process Of Mixed Plastic Waste Int. J. Adv. Eng. Technol 8 794–802
[10] Fakhrhoseini S M and M Dastanian 2013 Predicting pyrolysis products of PE, PP, and PET using NRTL activity coefficient model J. Chem 2013 7–9
[11] Bridgwater A V 2012 Review of fast pyrolysis of biomass and product upgrading Biomass Bioenergy 38 68–94
[12] Kreith F 2015 The CRC Handbook of Mechanica engineering, Second Edition. CRC Press, 2005.
[13] Abnisa F and Wan Daud W M A 2014 A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil Energy Convers Manage 87 71–85
[14] Sharuddin S D A, Abnisa F, Daud W M A and Aroua M K 2016 A review on pyrolysis of plastic wastes Energy Convers Manage 115 308–326
[15] Basu P 2010 Biomass gasification and pyrolysis: practical design and theory USA 2010
[16] Onwudili J A, Insura N and Williams P T 2009 Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time J. Anal. Appl. Pyrolysis 86 293–303
[17] Chen D, Yin L, Wang H and He P 2015 Reprint of: Pyrolysis technologies for municipal solid waste: A review Waste Manage 37 116–136
[18] Meyer R, Attanasi E and Freeman P 2007 Heavy Oil and Natural Bitumen Resources in Geological Basins of the World Us Geological Survey 36
[19] Khan M Z H, Sultana M, Al-Mamun M R and Hasan M R 2016 Pyrolytic Waste Plastic Oil and Its Diesel Blend : Fuel Characterization Journal of Environmental and Public Health
[20] Liaw H J, Tang C L and Lai J S 2004 A model for predicting the flash point of ternary flammable solutions of liquid Combustion and Flame 138 308–319
[21] Bozbas K 2008 Biodiesel as an alternative motor fuel: Production and policies in the European Union Renewable and Sustainable Energy Reviews 12 542–552
[22] Ahmad I 2015 Pyrolysis study of polypropylene and polyethylene into premium oil products International Journal of Green Energy 12 663–671
[23] M Kiple M, Giroids P, Fagla B, Anjorin M, Ziegler-Devin I and Y Rogaume 2017 Kinetic Study of Low Density Polyethylene Using Thermogravimetric Analysis Part 2: Isothermal Study Waste and Biomass Valorization 8 707–719
[24] Sharma S and Ghoshal A K, 2010 Study of kinetics of co-pyrolysis of coal and waste LDPE blends under argon atmosphere Fuel 89 12 3943–3951
[25] Kayacan I and Doğan O M 2008 Pyrolysis of Low and High Density Polyethylene. Part I: Non-isothermal Pyrolysis Kinetics A Part: Recovery, Utilization, and Environmental Effects Energy Sources 30 5 385–391