Kinetic modeling of LDPE Pyrolysis Using Coats-Redfern Method

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Abstract

Pyrolysis of polymer waste can potentially be a source of renewable energy, as it is a possible way to produce liquid fuel. In order to industrialize the process, the kinetic behavior of the pyrolysis has to be well understood. In this study, pyrolysis of virgin low density polyethylene (LDPE) was studied using thermogravimetric analysis (TGA). The test was carried out from 303-923 K at 20K/min in a nitrogen atmosphere. The TGA result was used to develop suitable models to calculate the activation energy, E, and pre-exponential factor, A, using Coats-Redfern method. Proximate and elemental analysis was also carried out on the LDPE sample. It was discovered that all reaction models were able to produce satisfactory linear fit of the data, with high correlation coefficients. Therefore, Coats-Redfern method cannot be used alone, but must be coupled with other methods to determine the correct reaction mechanism for the pyrolysis. By assuming first-order reaction, the calculated activation energy and pre-exponential factor are 166.75 kJ/mol and 4.97×10^{11} s^{-1}, respectively.

Keywords: *Low density polyethylene (LDPE), kinetic modeling, Coats-Redfern method, Thermogravimetric analysis (TGA), proximate and elemental analysis*

1.0 INTRODUCTION

While human is enjoying the benefits brought by fossil fuels as sources of energy, it is already known that such benefit is not long-lasting, due to its non-renewable nature. Thus, scientists are working hard to develop renewable energy sources, with the supports by government of different nations in various forms, including feed-in tariff.[1, 2] Among the available options, pyrolysis of polymer waste has received much attention, due to the possibility to harness the energy content in the waste in the form of liquid fuel. Such process is promising, as supported by several reviews in this field.[3-5] In the study of polymer pyrolysis, it is necessary to perform modeling to transform the reaction into mathematical equations, which then can be used to create simulations in the computer software for engineering purpose. In addition, the models enable engineers to virtually understand the process, while enabling optimization of the process, as well as reaction design.

In modeling of polymer pyrolysis, there are several kinetic modeling methods that are utilized by the researchers. Among the methods, non-isothermal thermogavimetry is a popular method to be used, due to its simplicity. In such method, data from Thermogravimetric analysis (TGA) of polymer is transformed to produce a linear plot, which is then used to calculate the activation energy and pre-exponential factor for the reaction. The objective of this study is to carry out kinetic modeling on pyrolysis of virgin low density polyethylene (LDPE) using Coats-Redfern method. Different reaction

models were applied on the data for comparison purpose, and the suitable value was determined for activation energy of the reaction.

2.0 EXPERIMENTAL

Virgin low density polyethylene (LDPE) in pellet form was purchased from Titan Chemicals in Johor, Malaysia. Prior to the study, the pellets had been grinded to produce powder in the size of ~700 μm. The dissolution behavior of the LDPE powder in compatible solvents was carried out for cracking purpose [6, 7]. Ultimate analysis was performed on LDPE powder by using vario MICRO cube from Elementar. For each testing, 2 mg of the sample was placed in the capsule, which was then put into the autosampler with excess oxygen. The sample was then heated to 990 °C in the presence of CuO as catalyst, and the resulting gas mixture from the sample, consisting CO2, H2O and NO_x, was separated in temperature programmed desorption (TPD) column. The amount of each gas was then quantified using a thermal conductivity detector (TCD).

   Proximate analysis of the LDPE sample was carried out using a benchtop furnace manufactured by NeyTech (model: D-130). The method from analysis was adopted from the work by Bemgba, Anwar, and Arshad [8]. Firstly, an empty crucible with cover was weighed using electronic balance. Then, 1g of sample of the LDPE powder was put in the crucible without cover, and heated in the furnace at 107 ^{o}C for 1 hour. The crucible was then taken out from the furnace and covered. After cooling, the crucible was weighed again at room temperature. The moisture content was calculated using formula (1). The remaining sample in the covered crucible was then heated again at 950 °C for 7 minutes. After that, the crucible was cooled to room temperature before weighing, and percentage of volatile matter in the sample was calculated using Equation (2). Finally, the sample was heated in covered crucible at 700 °C for 2 hours. After cooling, the crucible was weighed, and percentage of ash was determined using Equation (3). The percentage of fixed carbon was calculated according to Equation (4).

$$moisture\ content, \% = \frac{a-b}{a}\ x\ 100 \qquad (1)$$
$$volatile\ matter, \% = \frac{b-c}{a}\ x\ 100 \qquad (2)$$
$$ash\ content, \% = \frac{d}{a}\ x\ 100 \qquad (3)$$
$$fixed\ carbon, \% = 100\% - [\ moisture + volatile\ matter + ash\ content] \qquad (4)$$

Where
a   = initial weight of the sample,
b   = final weight of the sample after heating at 107 °C,
c   = final weight of the sample after heating at 950 °C, and
d   = final weight of the sample after heating at 700 °C.

   The thermal event of the polymer samples were studied in pyrolysis experiment, which was carried out in a TGA (TG 209 F3 Tarsus manufactured by Netzsch, Germany) under inert atmosphere. 3-6 mg of each sample was pyrolyzed under 100 cm^3 min^{-1} N_2 flow at heating rate of 20K/min from 30°C to 900°C. The small amount of sample and comparatively slow heating rate minimize the effect of heat transfer limitation on the pyrolysis process. From these assays, the sample weight loss with temperature (TG) and corresponding weight loss rate (DTG) were obtained from the pyrolysis. The weight loss rate was calculated based on Equation (5):

$$\frac{dW}{dt} = -\frac{1}{W_0}\left(\frac{dm}{dt}\right) \qquad (5)$$

where W_0 is the intial sample mass.

Usually the change in extent of reaction (α) is used to study the solid state reactions kinetics (Refer to Equation 6):

$$\alpha = \frac{m_o - m_t}{m_o - m_\infty} \qquad (6)$$

where m_0, m_t and m_∞ are initial sample mass, sample mass at time t and sample mass at the end of reaction, respectively. Using extent of reaction, the rate of a solid state reaction can be generally described as shown by Equation 7:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (7)$$

Integration of the above equation gives the integral rate law:

$$g(\alpha) = kT \qquad (8)$$

Several reaction models using $g(\alpha)$ are listed in Table 1. The explicit temperature dependence of the rate constant is introduced by replacing k(T) with the Arrhenius equation which gives

$$\frac{d\alpha}{dt} = A\exp(\frac{-E_a}{RT})f(\alpha) \qquad (9)$$

$$g(\alpha) = A\exp(\frac{-E_a}{RT})T \qquad (10)$$

where A (the pre-exponential factor) and E_a (activation energy) are the Arrhenius parameters. These parameters together with the reaction model are sometimes called the kinetics triplet. Under non-isothermal conditions, in which a sample is heated at a constant rate, the explicit temporal in Equation.(10) is eliminated through the trivial transformation:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp(\frac{-E_a}{RT})f(\alpha) \qquad (11)$$

Upon integration, Equation.(11) gives

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp(\frac{-E_a}{T})\,dT \qquad (12)$$

If $E_a/(RT)$ is replaced by x and integration limits transformed, Equation.(12) becomes

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2}\,dx \qquad (13)$$

Equation (12) can be written as

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2}\,dx \qquad (14)$$

p(x) has no analytical solution but has many approximations, with one of the most popular being the Coats-Redfern method. This method utilizes the asymptotic series expansion for approximating the exponential integral in Equation.(14), giving

$$ln\frac{g(\alpha)}{T^2} = ln[\frac{AE_a}{\beta R}\left(1 - \frac{2RT}{E_a}\right) - \frac{-E_a}{RT} \qquad (15)$$

In Coats-Redfern method, the suitable $g(\alpha)$ has to be chosen from a list of expressions, which is widely available in the kinetic studies on polymer samples [9]. Plotting the left hand side of Equation (15), which includes $g(\alpha)$, versus 1/T, gives E_a from the slope. By taking the temperature where $W=(W_o+W_t)/2$, in the place of the intercept term, the pre-exponential factor A can also be determined from Equation (15). The expression for $g(\alpha)$ used in this study in shown in Table 1. The model that gives the best linear fit is selected as the chosen model.

Table 1 Algebraic expression of functions of the most common reaction mechanisms.

Mechanism	g(x)
Power law (P2)	$x^{1/2}$
Power law (P3)	$x^{1/3}$

Power law (P4)	$x^{1/4}$
Avarami-Erofe'ev (A2)	$[-\ln(1-x)]^{1/2}$
Avarami-Erofe'ev (A3)	$[-\ln(1-x)]^{1/3}$
Avarami-Erofe'ev (A4)	$[-\ln(1-x)]^{1/4}$
Contracting Area (R2)	$[1-(1-x)^{1/2}]$
Contracting volume (R3)	$[1-(1-x)^{1/3}]$
One-dimensional diffusion (D1)	x^2
Two-dimensional diffusion (D2)	$[(1-x)\ln(1-x)]+x$
Three-dimensional diffusion (D3)	$[1-(1-x)^{1/3}]^2$
Ginstling-Brounshtein (D4)	$1-(2x-3)-(1-x)^{2/3}$
First-order reaction (F1)	$-\ln(1-x)$
Second-order Reaction (F2)	$(1-x)^{-1}-1$
Third-order reaction (F3)	$[(1-x)^{-2}-1]/2$

Table 2 Proximate and elemental analysis of LDPE.

Proximate Analysis	
Moisture Content	0.08
Volatile Matter	99.79
Ash Content	0.08
Fixed Carbon	0.05
Total	100.0

Elemental Analysis	
C	83.457
H	13.693
N	0.007
S	0.459
O	2.384 (by difference)
Total	100.0

3.0 RESULTS AND DISCUSSION

The TGA thermogram, as shown in Fig. 1, indicated that decomposition of virgin LDPE occurred in a single step pattern. Decomposition of LDPE started at 380 °C. Peak decomposition temperature was established at 471.9 °C and complete decomposition occurred around 560°C. The decomposition characteristics are consistent with most results of LDPE samples reported in the literature.[10] The TGA results have indicated the most suitable temperatures for the pyrolysis of LDPE for optimum yield. Based on the TGA data, the pyrolysis temperature was set to be 500 ℃, in order to achieve high conversion of LDPE.

In Coats-Redfern method, the suitable $g(\alpha)$ has to be chosen from a list of expressions, which is widely available in the kinetic studies on polymer samples.[9] When the reaction-order models were applied on Equation (11), the graphs were plotted as in Fig. 2, while the values of E_a and A are tabulated in Table 3. It is shown that almost all reaction models can be used on TGA data to produce plots with satisfactory correlation coefficients, when suitable range of the data is selected. The order of magnitude

of calculated activation energy is similar (17-500 kJ/mol) using all reaction models. However, the values of A vary in a wide range (10^1 -10^{29} s^{-1}) when different models are used in the calculation. Thus, Coats-Redfern method cannot be used independently to determine the correct reaction model of the pyrolysis. Instead, result from such method has to be validated by other methods, including isothermal method. Such conclusion was also made in other work.[9]

In literature, most researchers assume first-order reaction for polymer pyrolysis, as shown in Table 4. Therefore, the same model is used in this paper to decide on the numerical values of the E_a and A, which are 166.75 kJ/mol and 4.97 x 10^{11} s^{-1}, respectively. These values are in agreement with the literature, as summarized in Table 4. It is noted that there are many factors that affect the value of E_a, with the main factor being heating rate,[11] result in a widely range of calculated activation energies.
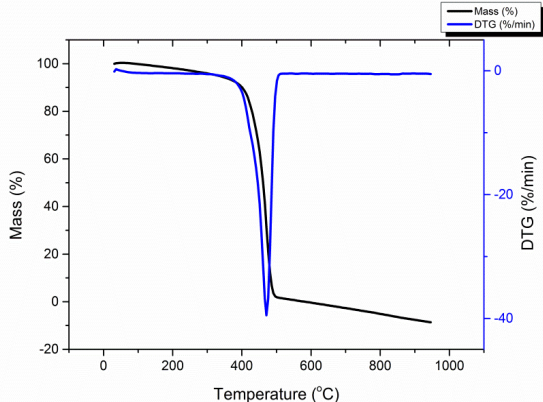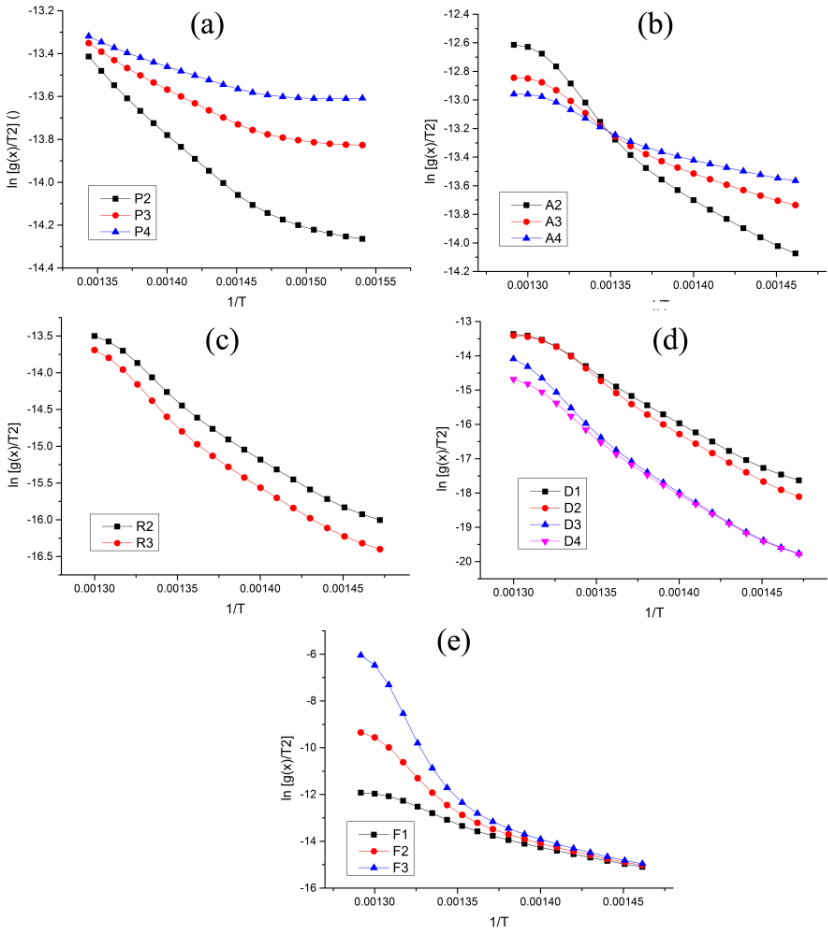

Figure 1 TG/DTG for virgin LDPE powder.

Figure 2 Plot of ln $[(g(x)/T^2]$ versus $1/T$ according to (a) power law; (b) Avarami-Erofe've models; (c) contracting sphere and cylinder models; (d) diffusion models and (e) reaction order models.

Table 3 Values of activation energy (E_a), pre-exponential factor (A) and correlation coefficient (R^2) for each model.

Reaction Model	E_a (kJ/mol)	A	R^2
Power law (P2)	46.01	3.61×10^2	0.9923
Power law (P3)	26.74	1.33×10^1	0.9903
Power law (P4)	17.12	3.27	0.9872
Avarami-Erofe'ev (A2)	76.45	1.12×10^5	0.9749
Avarami-Erofe'ev (A3)	46.99	9.95×10^2	0.9710
Avarami-Erofe'ev (A4)	32.26	4.50×10^1	0.9661
Contracting Area (R2)	247.91	8.08×10^{16}	0.9935
Contracting volume (R3)	127.37	1.95×10^8	0.9870
One-dimensional diffusion (D1)	138.60	4.21×10^9	0.9952
Two-dimensional diffusion (D2)	247.91	8.08×10^{16}	0.9935
Three-dimensional diffusion (D3)	283.48	7.35×10^{18}	0.9825
Ginstling-Brounshtein (D4)	260.59	1.28×10^{17}	0.9898
First-order reaction (F1)	166.75	4.97×10^{11}	0.9746
Second-order Reaction (F2)	268.64	3.11×10^{19}	0.9010
Third-order reaction (F3)	398.45	2.14×10^{29}	0.8388

Table 4 Literature for studies on polymer pyrolysis kinetics.

Reference	Materials	Reaction Mechanism	E_a (kJ/mol)
[12]	Virgin LDPE	Contracting Sphere (R2)	312
[13]	Raw LDPE	First order reaction (F1)	324-497
[11]	Raw LDPE	Contracting area (R2)	126-235
[14]	Virgin LDPE	Non-isothermal gravimetry	218
[15]	Virgin HDPE	First-order reaction (F1)	95.6-274.72
[16]	Virgin LDPE	First-order reaction (F1)	285.74

4.0 CONCLUSION

Kinetic modeling for pyrolysis behavior of virgin LDPE in TGA has been successfully carried out using Coats- Redfern method. It is shown that in such method, most reaction models can be applied to the TGA data to produce linear plots with high correlation coefficients, hence the correction reaction mechanism for LDPE pyrolysis cannot be determined solely by this method. Instead, other kinetic modeling methods have to be used for the purpose. By assuming first order reaction, the activation energy and pre-exponential factor for the pyrolysis of LDPE are 166.75 kJ/mol and 4.97×10^{11} s^{-1}.

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References
(1) Wong, S. L., Ngadi, N., Abdullah, T. A. T., Inuwa, I. M., 2015. *Renewable & Sustainable Energy Reviews.* 41: 42-52.
(2) Muhammad-Sukki, F., Abu-Bakar, S. H., Munir, A., Yasin, S. H. M., Ramirez-Iniguez, R., McMeekin, S. G., Stewart, B. G., Rahim, R. A., 2014. *Energy Policy.* 67: 618-625.
(3) Wong, S. L., Ngadi, N., Abdullah, T. A. T., Inuwa, I. M., 2015. *Renewable and Sustainable Energy Reviews.* 50: 1167-1180.
(4) Hossain, A. K., Davies, P. A., 2013. *Renewable & Sustainable Energy Reviews.* 21: 165-189.
(5) Al-Salem, S. M., Lettieri, P., Baeyens, J., 2010. *Progress in Energy and Combustion Science.* 36: 103-129.
(6) Wong, S. L., Ngadi, N., Abdullah, T. In *Study on Dissolution of Low Density Polyethylene (LDPE)*, Applied Mechanics and Materials, 2015; 2015; 170-173.
(7) Wong, S. L., Norzita, N., Abdullah, T. A. T. In *Solubilisation of Low Density Polyethylene (LDPE) for Pyrolysis*, 4th International Graduate Conference on Engineering Science & Humanity 2013, Universiti Teknologi Malaysia, Johor Bahru, Johor,Malaysia, 2013; Universiti Teknologi Malaysia, Johor Bahru, Johor,Malaysia, 2013; 1029-1035.
(8) Nyakuma, B. B., Johari, A., Ahmad, A., 2012. *Journal of Applied Sciences.* 12: 2527-2533.
(9) Ebrahimi-Kahrizsangi, R., Abbasi, M. H., 2008. *Transactions of Nonferrous Metals Society of China.* 18: 217-221.
(10) Renzini, M. S., Lerici, L. C., Sedran, U., Pierella, L. B., 2011. *Journal of Analytical and Applied Pyrolysis.* 92: 450-455.
(11) Sinfr, nio, F. S. M., Santos, J. C. O., Pereira, L. G., Souza, A. G., Concei, o, M. M., Fernandes Jr, V. J., Fonseca, V. M., 2005. *Journal of Thermal Analysis and Calorimetry.* 79: 393-399.
(12) Aboulkas, A., El Harfi, K., El Bouadili, A., 2010. *Energy Conversion and Management.* 51: 1363-1369.
(13) Kayacan, I., Dogan, O. M., 2008. *Energy Sources Part a-Recovery Utilization and Environmental Effects.* 30: 385-391.
(14) Aboulkas, A., El Harhi, K., El Bouadili, A., Nadifiyine, M., Benchanaa, M., Mokhlisse, A., 2009. *Fuel Processing Technology.* 90: 722-728.
(15) Khaghanikavkani, E., Farid, M. M., 2011. *Energy Science and Technology.* 2: 1-10.
(16) Encinar, J. M., Gonzalez, J. F., 2008. *Fuel Processing Technology.* 89: 678-686.