Kinetic Analysis of Polyethylene Terephthalate (PET) By Using TGA

Muhammad Ridzwan Bin Rosdi, Dr Rusmi Alias

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract*—This study provides the effect of temperature on mass change of plastic over time by using Thermogravimetric Analysis (TGA).The main objectives includes studying the thermal degradation and kinetic analysis of 20mg plastic Polyethylene terephthalate (PET). Thermal degradation was done by using a Thermogravimetric analyzer with temperature range from 25°C to 800°C at varies heating rates. Calculated kinetics parameters obtained by using Ozawa Flynn and wall (OFW) method are 86.764 KJ/mol for the activation energy (Ea) and 1.29x10^{10} min $^{-1}$ for the pre exponential factor (A).

Keywords*—Kinetics, Thermogravimetric analyzer (TGA), Polyethylene terephthalate (PET)

I. INTRODUCTION

As the population in Malaysia increase, the plastic consumption also increased. Plastic and the other solid waste usually disposed by two method which are landfilling and incineration .However this two method is no more relevant due to the lack of available land for dumping . Pyrolysis is thermal decomposition of materials at elevated temperature .By using pyrolysis technology a new product can be produced form the plastic waste and there will be energy recovery .Thermal degradation mechanism of plastic is complex as it involves with the changes in molecular weight of the material .Recycled plastic will going through continuous change of mass in temperature.. PET or Polyethylene terephthalate is a type of waste plastic and a combination of hydrocarbon, benzene and oxygen .PET plastic has high percentage of oxygen content. The kinetics of thermal degradation of PET must be analyzed to provide the apparent kinetic parameters that are useful for the optimal design and operation of pyrolysis process.

Thermal degradation of plastic can be measured by using Thermogravimetric Analyzer; the results from the analyzer will produce two types of graph which are thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). TGA curve will measured the weight change as the function of temperature and time in a controlled environment[1]. As for DTG, the curve will gave the information on degradation step occurred during the process [1].

Isoconversional method can be distinguished into two groups of methods where the first method (Type B) depends on approximating known as temperature integral and requires data on temperature, Tf *(β).* The other method (Type A) of isoconversional uses determination of the reaction rate at an equivalent stage of the reaction for various heating rate, the method under this set is the Friedman method [2].The isoconversional models used in this study is Ozawa Flynn and wall (OFW).

Therefore this study provides the effect of temperature on mass change of plastic over time by using Thermogravimetric Analysis (TGA).The main objectives includes studying the thermal degradation and kinetic analysis of plastic Polyethylene terephthalate (PET).

II. METHODOLOGY

A. Sample preparation

Polyethylene terephthalate (PET) that used in this study were obtained from waste bottle plastic waste of 1500 ml mineral water. The bottles were collected from the nearby area of UiTM Shah Alam campus .All the bottles were cleaned up with tap water to remove impurities and dirt before the bottles were left to dry in a room temperature .Then the bottle was cut into small pieces (approximately 1mm^2) and were kept in an airtight plastic with a PET label on it .After that, the sample that has been cut will be grinded by using polymer grinder to get a smaller type of sample.

B. Experimental Analysis

The study of Polyethylene terephthalate (PET) thermal degradation was done by using a Thermogravimetric analyzer. The temperature range is from 25°C to 800°C and the heating rates use are 10 °C/min, 20°C/min, 30°C/min and 40°C/min .Each run will be conducted with 20 mg of sample and four samples are required for four different heating rate .

The carrier gas used is Nitrogen gas with flow rate of 50 mL/min. Out of all those gases, Nitrogen is more preferable to be used as carrier gas in pyrolysis process as it was easier and safer to handle compare to the other carrier gases. Even Hydrogen produced the highest product yield, but Hydrogen has high reactivity that can lead to flammability hazard[3].

C. Kinetics method

The Thermogravimetric Analysis (TGA) data was converted to normalized mass, W by using Eq. (1).Where m = mass at a time m_0 = initial mass.

$$W = \frac{m}{m0} \tag{1}$$

Then the Derivative thermogravimetric analysis (DTG) curve was obtained by using TGA software and normalized (dW/dt) as Eq. (2).

$$\frac{dW}{dt} = \frac{dm}{dt}\frac{1}{m0} \tag{2}$$

Experimental conversion, α then was calculated by using Eq. (3).

$$\alpha\, exp = \frac{W0 - W}{W0 - Wf} \tag{3}$$

Where, W_0 is the normalized initial weight, W is the normalized mass at a time and W_f is the normalized mass at the end of volatile release. While, the experimental conversion rate, $(d\alpha/dt)_{exp}$ is given as Eq. (4).

$$\left(\frac{d\alpha}{dt}\right)exp = -\frac{dW}{dt}\frac{1}{(W0 - Wf)} \quad (4)$$

The theoretical conversion rate, $(d\alpha/dt)_{theoretical}$ is given by Eq. (5).

$$\left(\frac{d\alpha}{dt}\right)theoritical = k[f(\alpha)] = A[f(\alpha)][exp\left(\frac{E}{RT}\right)] \quad (5)$$

Then it rearranged to be as Eq. (6).

$$k = A[exp\left(\frac{E}{RT}\right)] \quad (6)$$

Where A = Pre-exponential factor, R = Universal gas constant (8.314 J/mol.K), E = Activation energy and T = Absolute temperature

D.Isoconversional method

Isoconversional method is a technique to calculate activation energy, the benefit of isoconversional method is the prediction of kinetic parameter (model free basis) without any reaction model (*f (α)*)[2][4]. The principle isoconversional method is at any constant conversion the reaction rate is a function of temperature as shown in Eq.(7) [5].

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = -\frac{Ea}{R} \quad (7)$$

The differential form of isoconversional method is representing as Eq. (8). Where β is heating rate for various temperature program[6].

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = ln\left(\beta\frac{d\alpha}{dT}\right)_{\alpha,i} = \ln[A_{\alpha}f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (8)$$

While the integral form for isoconversional method for non-isothermal temperature with constant heating rate, β can be represented as Eq.(9) [6].

$$g(\alpha) = \frac{A}{\beta}\int_0^t \exp\left(\frac{-Ea}{RT}\right)dT = \frac{A}{\beta}I(Ea,T) \quad (9)$$

Ozawa Flynn Wall (OFW) is a modified general isoconversional of Eq.(10) by Doyle where approximation of B = 0 and C = 1.052 [6],Then it becomes Eq.(11) .

$$\ln\left(\frac{\beta i}{T^{B}_{\alpha,i}}\right) = const. - C\left(\frac{E\alpha}{RT\alpha}\right) \quad (10)$$

Activation energy (*Ea*) can be obtained from the plot of left hand side of slope and *1/Tα* can be obtained by using all the heating rates of isoconversional principle [6].

$$\ln(\beta_{i)} = Const - 1.052\frac{Ea}{RTa} \quad (11)$$

III. RESULTS AND DISCUSSION

Table 1: Proximate Analysis Of PET [7], [8]

Type of plastic	Moisture (Wt %)	Fixed Carbon (wt %)	Volatile (Wt %)	Ash (Wt %)
Polyethylene terephthalate (PET)	0.46	7.77	91.75	0.02

Table 2: Net Calorific Value and Ultimate Analysis Of PET [9]

Net calorific value (MJ /Kg)	21.85
	Weightage (wt %)
C	62.2
H	4.2
N	0
O	±33.6

The proximate analyses of the sample (PET) are shown in Table 1 and the calorific value and Ultimate analysis of PET are shown in Table 2.

A. TGA Analysis

The result for Thermogravimetric analysis (TGA) and Derivative thermos-gravimetric (DTG) at four different heating rate of 10 °C/min, 20°C/min, 30°C/min and 40°C/min with temperature range from 25°C to 800°C are shown in Fig.2 .Table 3 show the initial weight (mg) ,Heating rate (°C/min) ,Temperature range (°C) ,Onset Temperature (T*o*) ,End Temperature (T*e*) and Maximum degradation rate Temperature (T*m*). Figure show the calculation step for T*o,* T*e* and T*m*.

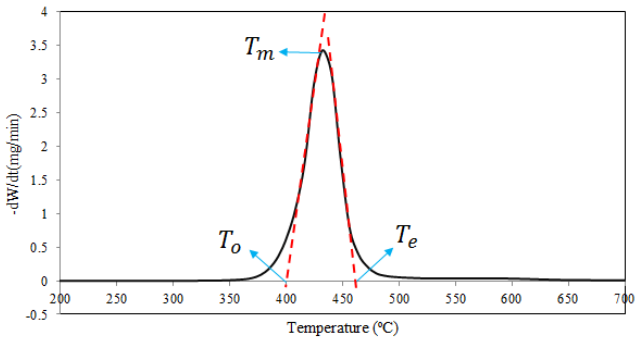


Fig 1: Step for Onset Temperature (T*o*), End Temperature (T*e*) and Maximum degradation rate Temperature (T*m*) estimation from DTG [6].

From table 3, the Onset temperature (T*o*), End temperature (T*e*) and Peak temperature (T*m*) increase as the heating rate increase .At heating rate of 10 °C /min, 20 °C /min, 30 °C /min and 40 °C /min, the Peak temperature (T*m*) are 431.0 °C , 447.6 °C, 456.9 °C and 460.1 °C .Different heating rate may affect the peak temperature for the weight loss [10].Lower heating rate make equilibrium take longer time to reach as gas is slowly purge to the sample .Higher heating rate tends to delay the degradation rate but shorten the reaction rate. Thus, it will affect the onset temperature (T*o*), end temperature (T*e*) and maximum degradation rate temperature (T*m*) by shifting the value to the right of the graph [11]

From Figure 2, it show that varies heating rate do not affect the shape of weight loss curve of TGA .The pattern for the TGA curve is same but slightly different in term of weight loss value (mg).

Table 3 TGA analysis: Temperature range (°C), Onset Temperature (T*o*), Temperature (T*m*).

Initial weight,(mg)	Heating rate, (°C/min)	Temperature range,(°C)	Onset Temperature, *To*(°C)
20	10	25-800	406.8
20	20	25-800	418.8
20	30	25-800	423.9
20	40	25-800	424.6

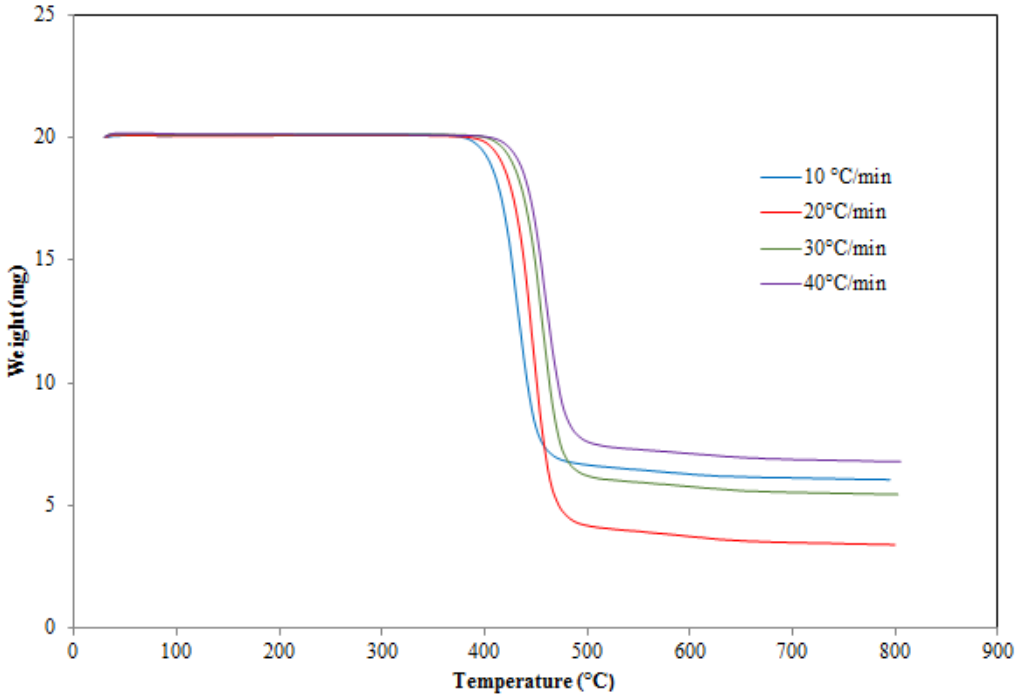


Fig. 2 : Weight loss (mg) versus temperature (ºC) for varies heating rate (10 °C/min, 20°C/min, 30°C/min and 40°C/min)

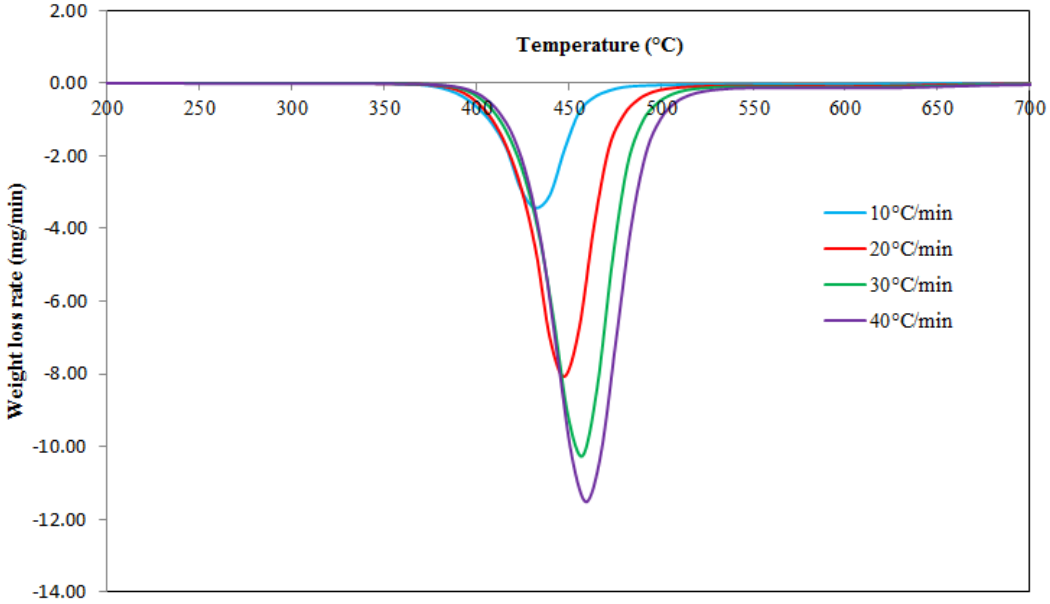


Fig 3: Derivative Thermogravimetric analysis (DTG) result at varies heating rate.

From the TGA result ,from temperature of 25 °C until 380 °C there is no great variation of the graph .At temperature of 400 °C the degradation process of PET start to occur and it show significant drop of weight until 490 °C .PET lost approximately 66 % to 83 % from the total weight in a single stage degradation .After the degradation process the remaining solid residue in

percent over the total initial weight for heating rate of 10 °C /min, 20 °C /min, 30 °C /min and 40 °C /min are 30.3 % ,17.1 %, 27.3 % and 34 % respectively .The remaining solid for each heating rate show huge differences in percent between each other .Supposedly the remaining solid residue should be slightly difference between each other even for a different heating rate .These outcomes is may be due to the heat transfer supply from furnace is provided efficiently to the sample [10].

Heating rate of 10 °C /min is the lowest heating rate parameter used for the process. However from the figure 2, the heating rate of 10 °C /min overlaps with 20 °C /min and 30 °C /min .This error can be due to the interruption from the noise of signal. This result show that it is something that not suppose naturally exist but can happen throughout the process .In details ,heat transfer from the sample to crucible or from crucible to sensor could be the factor to the artefact [10].

B. Kinetic Analysis

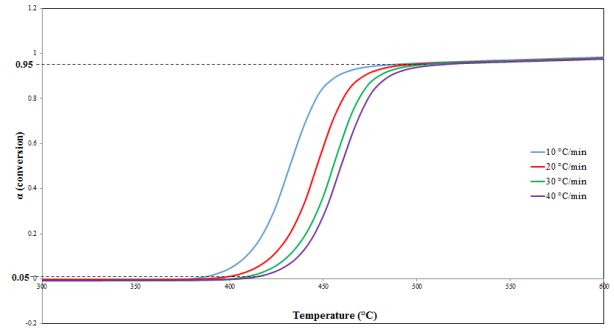
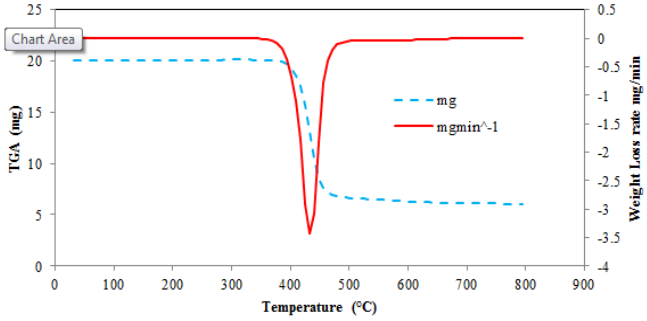
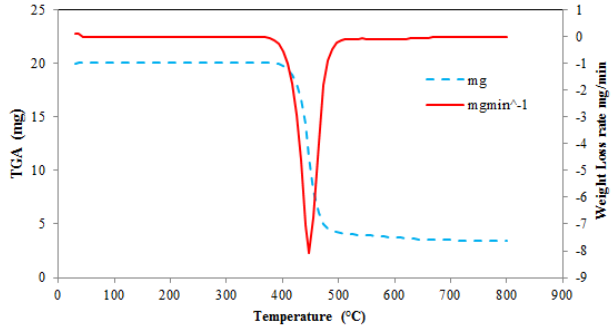


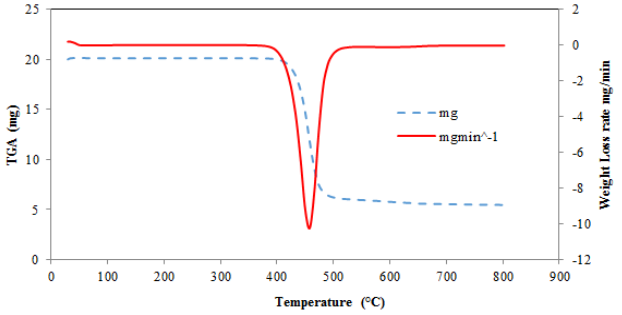
Fig 4: Extent of conversion for PET



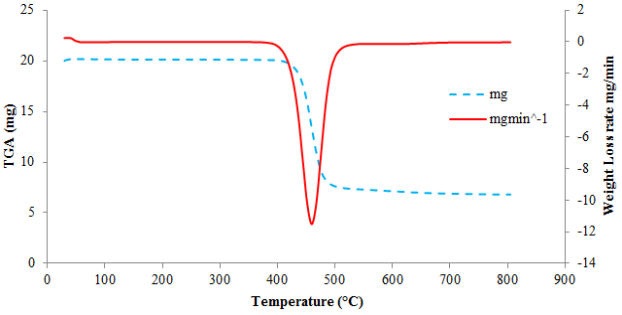
(a)



(b)



(c)



(d)

Figure 5: TGA and DSC result for heating rates 10 °C/min (a), 20 °C/min (b) ,30 °C/min (c), 40 °C/min (d)

Activation energy (Ea) and pre-exponential factor (A) were determined by using Ozawa Flynn Wall (OFW) method. First step in determining the kinetic parameter is to calculate the conversion or abbreviated as 'alpha' (α) of PET weight throughout degradation [12].

Conversion (α) is calculate by using eq. 3 .From figure 4 ,the extent of reaction have significant change between α from 0.05 to 0.95 .So by using interval of 0.1 ,the selected value of α are 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85 and 0.95.

Then values for activation energy (Ea) and pre-exponential factor (A) is obtain by plotting graph ln (β) versus 1/T ($°C^{-1}$) for different value of α.

Table 4 Parameter obtained from figure 4, (gradient, y-intercept or C and R^2)

α	m	R^2	C
0.05	-10879.0	0.9958	30.206
0.15	-8971.7	0.9967	24.161
0.25	-9576.7	0.9939	25.128
0.35	-9465.2	0.9813	24.588
0.45	-9851.0	0.9943	25.249
0.55	-9787.0	0.9910	24.922
0.65	-10211.0	0.9943	25.653
0.75	-10167.0	0.9979	25.347
0.85	-11114.0	0.9953	27.102
0.95	-11909.0	0.9990	28.182

From figure 6, gradient (m), y-intercept (c) and correlation coefficient (R^2) were obtained and recorded in table 4.From the gradient, activation energy (Ea) and pre exponential factor (A) for each conversion is obtained by implying straight line equation which is "y=mx+C". R^2 which represent correlation coefficient show the dependence of variable y (conversion) to the variable x (temperature).R^2 has varies value from 0 to 1, 0 mean low of dependence and 1 mean strong dependence [10].

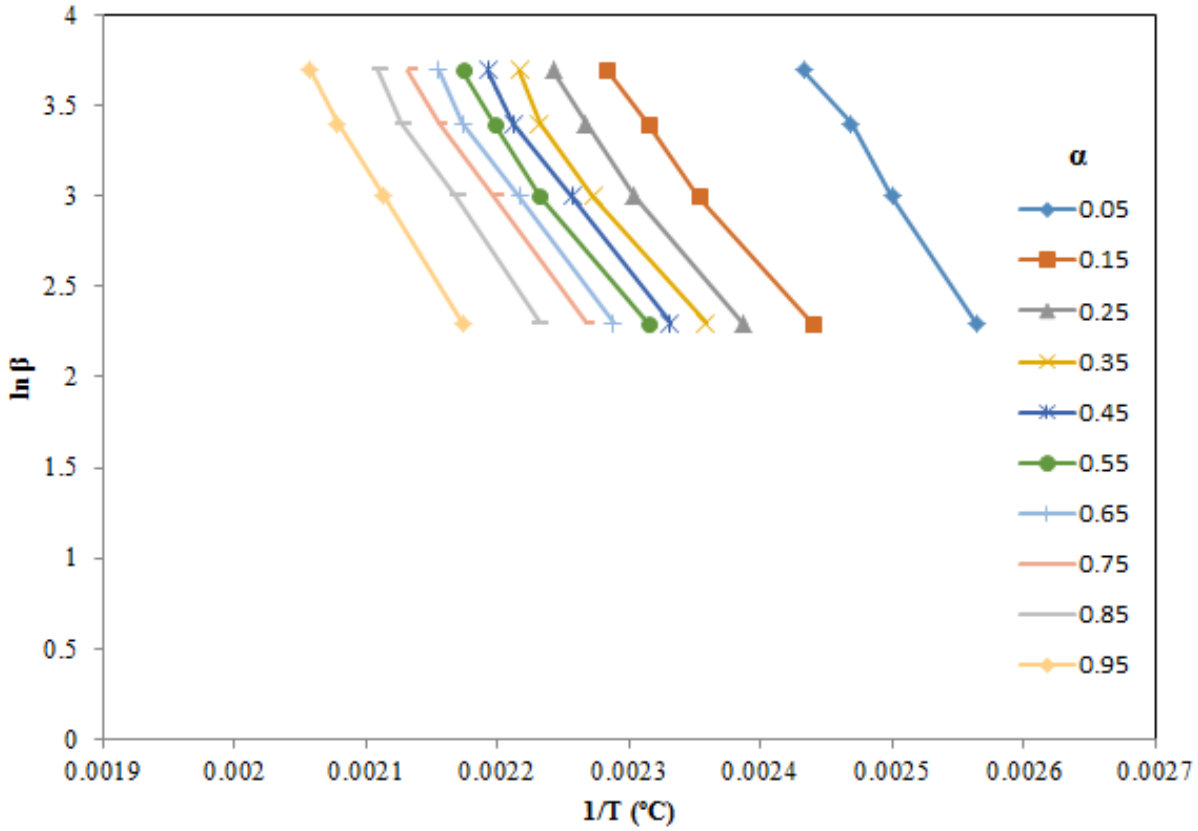


Fig 6: Regression line of Ozawa Flynn Wall (OFW) method

Table 5 Table for kinetic parameters result

PET Conversion (α)	Ozawa Flynn Wall (OFW) method		
	Ea (KJ/mol)	A (min^{-1})	R^2
0.05	92.762	1.25×10^{10}	0.9958
0.15	76.080	1.14×10^{8}	0.9967
0.25	81.372	4.97×10^{8}	0.9939
0.35	80.397	4.39×10^{8}	0.9913
0.45	83.771	1.13×10^{9}	0.9943
0.55	83.211	1.10×10^{9}	0.9910
0.65	86.920	2.89×10^{9}	0.9943
0.75	86.535	2.80×10^{9}	0.9979
0.85	94.818	2.03×10^{10}	0.9953
0.95	101.770	8.77×10^{10}	0.9990
Average	**86.764**	**1.29×10^{10}**	**0.9940**

The average value of Activation energy (Ea) for PET is 86.764 KJ/mol. Activation energy is the minimum amount of energy required chemical bond to break .The higher value of Ea mean higher energy required to breaks bond and at same time it is the factor for a slower reaction .From alpha (α) or conversion of 0.05 to 0.95 with the interval of 0.10 .The value of Ea does have significant change in between. This result shows that for every different Ea value for different conversion, the reaction mechanism for degradation is varied. This proved that, degradation process and the activation energy is dependence to conversion [13].The lowest activation energy value throughout the process is at α of 0.15 and the highest recorded activation energy value is at α equal to 0.95.From α of 0.35 to 0.95 the activation energy is increase.

Then for the value of correlation coefficient (R^2) from α equal to 0.05 to 0.95, the values range from 0.9910 to 0.9990.From the value, it is proved that there is strong correlation between variable x and y.

Based from study by B.G.GIRIJA et(2005)[14] the activation energy obtained for pure PET(Polyethylene terephthalate) is 227 KJ/mol with maximum weight loss at 60% .The temperature range used for the process is from 100ºC to 600 ºC and the

IV. Conclusion

TGA was confirmed to be suitable equipment for kinetic parameters determination for thermal degradation of polyethylene terephthalate (PET) at four different heating rates (10 °C /min, 20 °C /min, 30 °C /min and 40 °C /min).

The kinetic parameters, activation energy (Ea) and pre exponential factor (A) were able to be determined by using Ozawa Flynn Wall (OFW) method as the isoconversional method .With the range of conversion (α) from 0.05 to 0.95 ,the result obtained for the activation energy (Ea) and pre exponential factor (A) are 86.764 KJ/mol and 1.29×10^{10} min^{-1} respectively .

Acknowledgment

Foremost, I would like to express my sincere gratitude to my Supervisor Dr. Rusmi Alias for the continuous support for my study and also I would like to thanked my Faculty of Chemical Engineering of Universiti Teknologi Mara for support

REFERENCES

[1] S. Kumar and R. K. Singh, "Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis," *Brazilian J. Chem. Eng.*, vol. 28, no. 4, pp. 659–667, 2011.

[2] M. J. Starink, "The determination of activation energy from linear heating rate experiments: A comparison of the accuracy of isoconversion methods," *Thermochim. Acta*, vol. 404, no. 1–2, pp. 163–176, 2003.

[3] H. Zhang *et al.*, "A review on pyrolysis of plastic wastes," *Energy Convers. Manag.*, vol. 3, no. 17, p. 5769, 2013.

[4] J. R. Opfermann, E. Kaisersberger, and H. J. Flammersheim, "Model-free analysis of thermoanalytical data-advantages and

limitations," *Thermochim. Acta*, vol. 391, no. 1–2, pp. 119–127, 2002.

[5] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, and N. Sbirrazzuoli, "ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data," *Thermochim. Acta*, vol. 520, no. 1–2, pp. 1–19, Jun. 2011.

[6] P. Das and P. Tiwari, "Thermal degradation kinetics of plastics and model selection," *Thermochim. Acta*, vol. 654, no. October, pp. 191–202, 2017.

[7] F. Abnisa and W. M. A. Wan Daud, "A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil," *Energy Convers. Manag.*, vol. 87, pp. 71–85, 2014.

[8] F. Zannikos, S. Kalligeros, G. Anastopoulos, and E. Lois, "Converting Biomass and Waste Plastic to Solid Fuel Briquettes," *J. Renew. Energy*, vol. 2013, pp. 1–9, 2013.

[9] I. Martı, "Kinetic model for the pyrolysis and combustion of poly- (ethylene terephthalate) (PET)," vol. 59, pp. 635–650, 2001.

[10] G. Tondl, L. Bonell, and C. Pfeifer, "Thermogravimetric analysis and kinetic study of marine plastic litter," *Mar. Pollut. Bull.*, vol. 133, pp. 472–477, 2018.

[11] C. Quan, A. Li, and N. Gao, "Thermogravimetric analysis and kinetic study on large particles of printed circuit board wastes," *Waste Manag.*, vol. 29, no. 8, pp. 2353–2360, 2009.

[12] J. M. Encinar and J. González, *Pyrolysis of synthetic polymers and plastic wastes. Kinetic study*, vol. 89. 2008.

[13] C. Gai, Y. Dong, and T. Zhang, "Bioresource Technology The kinetic analysis of the pyrolysis of agricultural residue under non-isothermal conditions," *Bioresour. Technol.*, vol. 127, pp. 298–305, 2013.

[14] B. G. Girija, R. R. N. Sailaja, and G. Madras, "Thermal degradation and mechanical properties of PET blends," *Polym. Degrad. Stab.*, vol. 90, no. 1, pp. 147–153, 2005.