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Thermal Pyrolysis of Polyethylene: Kinetic Study

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Brief Introduction of the authors

First author is Elham Khaghanikavkani, Ph.D candidate at the University of Auckland (Department of Chemical and Materials Engineering) in New Zealand. She holds a B.Sc degree in chemical engineering (1994-1999) and M.Sc degree in petroleum engineering (2000-2003) both from Iran. Currently, she is conducting a research programme on the microwave pyrolysis of plastics for production of fuel funded by Foundation Research and Science Technology (FRST). Note that his research has been supervised by Professor Mohammed M. Farid (personal chair).

Professor Mohammed Farid obtained his PhD and MSc in Chemical Engineering from the University of Swansea, Wales and his BSc in Chemical Engineering from the University of Baghdad. He worked as a full professor in the Jordan University of Science and Technology, the University of Science Malaysia and since 1997 in The University of Auckland, New Zealand. He has published more than 250 papers in international journals and refereed international conferences, 6 patents, 5 books and 10 chapters in books. Farid has received a number of international awards and is a member of the editorial board of three international journals. He is a world leader in energy storage with phase change and has provided significant contribution to the field worldwide.

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Abstracts

Thermogravimetric analysis (TGA) was used to measure the kinetic parameters of high density polyethylene in different operating conditions i.e. heating rate and nitrogen flow rate in a non isothermal condition. The Coats-Redfern method was used to calculate the kinetic parameters. An effort was made to investigate the effect of metal particles on plastic during pyrolysis. The results suggested that aluminum powder accelerates the pyrolysis reaction by enhancing the heat transfer. In addition, the kinetic reaction of pyrolysis was studied using a semi-batch reactor in a nitrogen atmosphere under isothermal and non-isothermal conditions. A first-order decomposition reaction was assumed and the rate constant was determined using an integral method. The rate constant was measured at different temperatures and was used to calculate the apparent activation energy and the pre-exponential factor of the reaction in an isothermal condition. Kinetic parameters were measured for individual compounds with carbon numbers ranging from C_9 to C_{50} using the semi batch reactor under isothermal condition.

Key words: Kinetic; High density polyethylene; Isothermal; Non isothermal; TGA; Semi batch reactor

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NOMENCLATURE

M initial weigh of sample
m_t weigh of sample at time t
E_a activation energy (J/mol)
R universal gas constant (8.314 J/mol.K)
K_o pre-exponential factor (1/sec)
X_i conversion
N_i mol of the each carbon number
N_t total mol
F_l liquid fraction flow rate (ml/min)
C_i concentration (mol/ml)
t_i time interval (sec)
t_0 time at steady state temperature (sec)
n number of taken samples during the pyrolysis
s the lowest recognized carbon number in the liquid fraction
m the highest recognized carbon number in the liquid fraction

INTRODUCTION

There have been kinetic studies done of the thermal degradation of plastics waste by various researchers (Ballice, L., 2001; Bockhorn, H., Hentschel, J., Hornung, A., & Hornung, U., 1999a; Bockhorn, H., Hornung, A., Hornung, U., & Schawaller, D., 1999b; Conesa, J.A., Font, R., Marcilla, A., & Caballero, J.A., 1997; Conesa, J.A., Marcilla, A., & Font, R., 1994; Constable, D., Raner, K., Somlo, P., & Strauss, C., 1992; Costa, P.A., Pinto, F.J., Ramos, A.M., Gulyurtlu, I.K., Cabrita, I.A., & Bernardo, M.S., 2007; Elordi, G., Lopez, G., Olazar, M., Aguado, R., & Bilbao, J., 2007; Encinar, J.M. &Gonzalez, J.F., 2008; Encinar, J.M. &González, J.F., 2008; Ramdoss, P.K. &Tarrer, A.R., 1997, 1998; Ranzi, E., Dente, M., Faravelli, T., Bozzano, G., Fabini, S., Nava, R. et al., 1997; Westerhout, R.W.J., Waanders, J., Kuipers, J.A.M., & van Swaaij, W.P.M., 1997). Review of the kinetic parameters (Westerhout, R.W.J. et al., 1997) and methods of analysis (Petrovic, Z.S. &Zavargo, Z.Z., 1986) are well documented in the literature. In a majority of the studies a standard power law kinetic model was assumed to describe the pyrolysis rate of PE and PP (Ballice, L., 2001; Bockhorn, H. et al., 1999b; Ramdoss, P.K. &Tarrer, A.R., 1997). The measured values of activation energy and the pre-exponential factor for PE were between 160 to 320 kJ/mol and 10^{11} to 10^{21} (1/sec) respectively (Costa, P.A. et al., 2007), while other studies presented activation energy values as high as 498 kJ/mol (Kayacan, I. & Dogan, O.M., 2008). Undoubtedly TGA was the most commonly applied technique to evaluate kinetic parameters. Mass loss curves obtained by TGA have been analysed by different integral and differential methods. The reliability of the applied methods depends on the accuracy of the assumptions and the simplification of formulas (Petrovic, Z.S. &Zavargo, Z.Z., 1986). Detailed analysis of degradation steps i.e. initiation, β-scission, hydrogen transfer and termination (Bockhorn, H. et al., 1999b; Mastral, J.F., Berrueco, C., & Ceamanos, J., 2007; Ranzi, E. et al., 1997; Westerhout, R.W.J. et al., 1997) have been addressed. Investigation into the kinetic parameters based on distillation of products into high molecular weight, low molecular weight, solid and gas fractions (Conesa, J.A. et al., 1997; Costa, P.A. et al., 2007; Cozzani, V., Nicolella, C., Rovatti, M., & Tognotti, L., 1997) has been well addressed.

Kinetic studies have been done applying both isothermal and non isothermal measurements (Bockhorn, H. et al., 1999b; Ceamanos, J., Mastral, J.F., Millera, A., & Aldea, M.E., 2002; Encinar, J.M. &Gonzalez, J.F., 2008). The majority of these studies reported that the kinetic parameters obtained from isothermal measurements were not confirmed by non isothermal measurements. In 1999, analysis of isothermal kinetic study to determine the overall degradation of polyolefins using on-line mass spectrometry was performed by Bockhorn, H , Hornung, A, Hornung, U, and Schawaller, D.. The calculated activation energy and the pre-exponential factor were found to be 268±3 kJ/mol and 6E+17 (1/min) in a temperature range of 430°C to 480 °C for polyethylene. The results revealed that the apparent reaction order increases with temperatures from 0.8 to 1.4. They believed that heat transfer has less impact on sample thickness in isothermal conditions compared to non isothermal conditions. Ceamanos, J., Mastral, J.F., Millera, A., & Aldea, M.E (2002) compared the two methods of measurement and explained the possibility of using a simple first-order equation to enlighten the complex degradation mechanism of plastic. They obtained very different values 248.7 kJ/mol and 1.75E+17 (1/min) from the isothermal experiments and 346 kJ/mol and 2.53E+24 (1/min) from non isothermal experiments. Other study (Gao, Z., Amasaki, I., & Nakada, M., 2003b) found excellent conformity between results i.e. 201 kJ/mol for non isothermal and 194.8 kJ/mol for isothermal by using an iso-conversional method and assuming reaction order of 0.55. Sinfronio, F. S. M. et al. (2005) studied non isothermal decomposition, applying different kinetic methods such as the Flynn-Wall-Ozawa method, the Van Krevelen method, the Horowitz-Metzger method, the Coats-Redfern method, the Madhusudanan method and the Vyazovkin method. The lowest and highest reported values of activation energy were 126 kJ/mol and 275 kJ/mol for heating rate of 5°C/min, 10°C/min and 20°C/min. The Coats-Redfern method was found to describe best the decomposition reaction.

This paper presents the values of activation energy and the pre-exponential factor for HDPE obtained in isothermal and non isothermal conditions, assuming first order reaction kinetic using a semi batch reactor as well as TGA apparatus. The paper also highlights the most important reason for the variation of kinetic parameters obtained through TGA analysis in the published literature. Moreover, kinetic parameters were calculated for the first time for individual compounds with carbon number ranging from C_9 to C_{50} using the semi batch reactor.

1. MATERIALS AND INSTRUMENTS

In this study, the following materials and instruments were used:

1.1 High Density Polyethylene (HDPE)

Virgin high density polyethylene (HDPE) was obtained from Dow Chemical Company (Auckland, New Zealand) with density of 0.96 g/cc, melting point of 133°C, and melting index of 9 g/10 min. The diameter of virgin plastics in pellet form ranged from 2 mm to 3 mm.

1.2 GC/FID

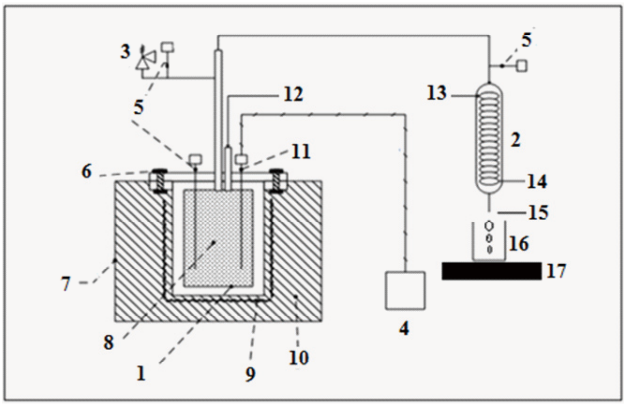
The oil/wax from pyrolysis of HDPE was analysed in gas chromatography flame ionisation detection equipment (GC/FID). Shimadzu17A was utilized for oil/wax analysis with an auto S/SL (Split/Splitless) injector. The capillary column was a MXT-Biodiesel TG, 15 m length × 0.32 mm internal diameter with 0.1 μm thickness. The programmed temperature was 50°C followed by a 15°C/min heating rate up to 395°C. The dwell time was 5 min at 395°C. 0.015 gram of the oil/wax products was dissolved in 5ml carbon disulfide.

1.3 TGA

A kinetic study was performed by a thermo-gravimetric analyser using a TGA-50 Shimadzu apparatus under non isothermal conditions. In addition to the detailed analysis of the pyrolysis conducted in the semi batch reactor as described in the next section, the HDPE samples were placed in pellet form in the aluminum sample holder of the TGA, running in a nitrogen atmosphere. Degradation of HDPE was carried out at different heating rates of 1°C/min, 3°C/min, 20°C/min and at nitrogen flow rates of 20, 50, 100 ml/min at 590°C with the mass of 15.5±0.5 mg. Later HDPE powder was pyrolysed after having been mixed with aluminum powder in an effort to improve temperature distribution in the sample, as will be explained in this paper.

1.4 Experiment

In this study, the pyrolysis of HDPE was performed in a semi-batch reactor at atmospheric pressure. Oil/wax yield refers to condensable products in this study. Scheme 1 shows the schematic diagram of the thermal pyrolysis setup. It consists of the following sections: (1) a stainless steel reactor with 67 mm diameter and 100 mm height, externally heated by 1kW rated coil surrounded with an insulation material to minimise heat loss, (2) a glass coil type condenser of 20 cm length, (3) a pressure relief valve (rupture disk type with aluminum foil) installed on the outlet of the reactor, and (4) a Proportional-Integral-Derivative (PID) temperature controller, also a data acquisition system and Pico logger software. Online temperature monitoring was performed using K-type thermocouples fixed at the inlet of the condenser and inside the reactor. When the temperature of the reactor reached the degradation temperature the generated gaseous products were condensed using the condenser. Note that gas and wax products came out of the same port, but wax products were collected in a container beneath the condenser and gases were vented to fume hood. All of the condensed products including wax inside the condenser and collection container were analysed all together. The experiment duration after the reactor reached desired temperature was 15 min. 0.7L/min of the nitrogen flow rate was used to purge the air and later to prevent any secondary reactions.



Scheme 1
Schematic of Pyrolysis Experimental Setup:
1-Removable Stainless Steel Reactor, 2-Condenser 3-Pressure Relief Valve, 4-PID Temperature Controller, 5-Thermocouple Connected to Picologger, 6-Bolted Flange, 7-Stainless Steel Shell, 8-Plastic Reactant, 9-Heating Coil (1kw), 10-Insulation, 11-Thermocouple Connected to PID Temperature Controller, 12-N_2 Inlet, 13-Circulating Water (Inlet), 14-Circulating Water (Outlet), 15-Gas Exhaust, 16-Product Collection Bin, 17-Balance.

2. KINETIC STUDY USING SEMI BATCH REACTOR

The overall activation energy and pre-exponential factor for the pyrolysis reaction were calculated under isothermal and non isothermal conditions using the semi batch reactor used in this work. Moreover, kinetic parameters were calculated, for the first time, for individual compounds with carbon number ranging from C_9 to C_{50} in isothermal condition. Diagram 1 shows the path of experiments using a semi batch reactor. Note that all presented results in this paper are the arithmetic mean of three runs with less than 5 percent error.

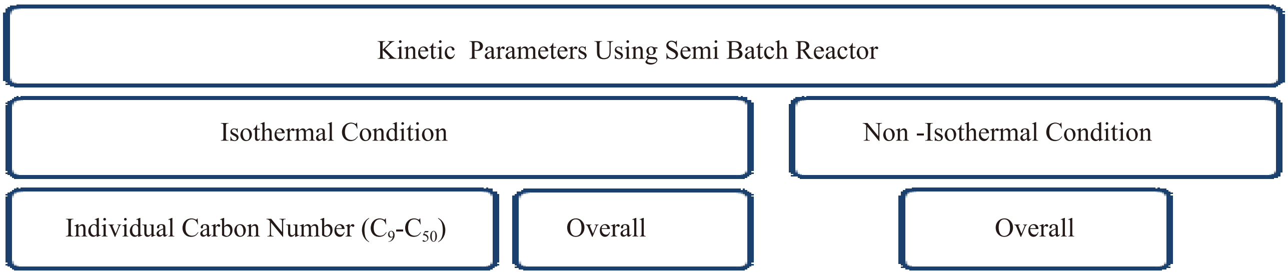


Diagram 1
Path of Experiments Using Semi Batch Reactor

2.1 Isothermal Condition

2.1.1 Individual Carbon Number

Activation energy and pre exponential factor values were calculated for individual carbon numbers ranging from C_9 to C_{50}. GC/FID was used for measuring the concentration of the product samples removed from the reactor at different times at different steady state temperatures. Experiments were run at three steady state temperatures (477°C, 466°C and 455°C) in the presence of 0.7 L/min N_2 flow rate. Conversion of each carbon number based on the liquid fraction is obtained from Equation 1 for individual carbon numbers.

$$X_i = N_i / N_t \qquad (1)$$

Where X_i is conversion, N_i is mol of the each carbon number and N_t is total mol.

Ni can be calculated from Equation 2.

$$N_i = F_l \ \Sigma_{i=1}^{i=n}(C_i \times t_i) \qquad (2)$$

Where F_l is flow rate of condensed gases fraction (ml/sec), C_i is their concentration (mol/ml), t_i is time interval (sec) and n is the number of samples collected during pyrolysis.

N_t is determined from Equation 3, where s and m are the lowest and highest recognised carbon numbers in liquid fractions.

$$N_t = F_l \ \Sigma_{j=s}^{j=m} \left(\Sigma_{i=1}^{i=n} \left(C_{i,j} \times t_i \right) \right) \qquad (3)$$

The kinetic Equation 4 was used for the calculation of isothermal conditions based on first order kinetic reaction, which on integration gives Equation 5. The reaction rate was calculated for every temperature for individual carbon numbers by plotting the $-\ln[(1-x)/(1-x_0)]$ versus $(t-t_0)$. Figure 1 shows the result for the carbon number 24 at 466 °C. The slope of the plot is the rate constant of the reaction coefficient at 466°C. The reaction rate constant is found from the slope of the curve. Acceptable R^2 was obtained for all applied temperatures and carbon numbers. The activation energy and the pre-exponential factor were calculated by plotting lnk versus reciprocal of temperature using Equation 7. Figure 2 shows the calculation of kinetic parameters for carbon number C_{24}.

$$\frac{dx}{dt} = k(1-x) \qquad (4)$$

$$\int_{x_0}^{x} \frac{dx}{1-x} = \int_{t_0}^{t} k dt \qquad (5)$$

$$-\ln \frac{1-x}{1-x_0} = k(t-t_0) \qquad (6)$$

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

Reported values of kinetic parameters for different carbon numbers ranging from C_9 to C_{50} in Table 1 reflect the gradual fluctuation of activation energy with carbon number with the highest and lowest values of 116 kJ/mol and 226 kJ/mol.

Table 1
Kinetic Parameters in Presence of N_2 Flow Rate under Isothermal Condition Using Semi Batch Reactor

Carbon No.	Ea (kJ/mol)	K_0 (1/sec)	Carbon No.	E_a (kJ/mol)	K_0 (1/sec)
9	164.15	4.89E+07	30	226.96	2.02E+11
10	142.30	1.45E+06	31	226.96	2.02E+11
11	142.09	1.35E+06	32	225.54	1.27E+11
12	146.69	2.58E+06	33	142.30	1.45E+05
13	163.69	4.22E+07	34	164.15	4.90E+06
14	116.68	1.57E+04	35	149.19	4.90E+06
15	136.94	4.20E+05	36	188.57	2.51E+08
16	117.17	1.47E+04	37	188.57	2.51E+08
17	123.74	4.32E+04	38	216.26	2.17E+10
18	142.68	8.17E+05	39	216.04	2.03E+10
19	121.04	2.33E+04	40	210.77	7.38E+09
20	142.76	6.72E+05	41	169.71	8.64E+06
21	174.54	9.56E+07	42	142.99	9.06E+04
22	142.89	5.26E+05	43	142.99	9.06E+04
23	188.94	7.08E+08	44	142.68	8.17E+04
24	188.94	7.08E+08	45	188.94	1.42E+08
25	143.13	3.79E+05	46	188.57	1.25E+08
26	143.13	3.79E+05	47	166.94	3.58E+06
27	137.51	1.32E+05	48	142.76	6.72E+04
28	226.96	2.02E+11	49	142.30	5.79E+04
29	226.96	2.02E+11	50	173.95	7.90E+06

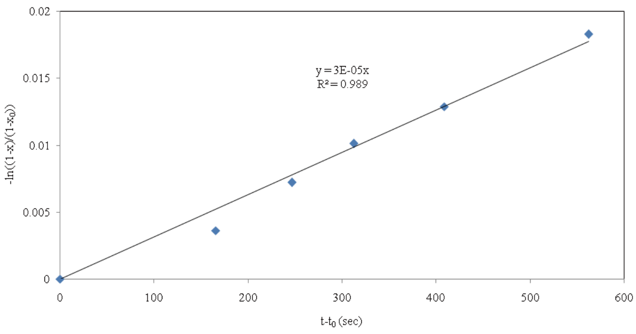


Figure 1
–ln [(1-x)/(1-x$_0$)] as a Function of Time for C$_{24}$ at 466°C

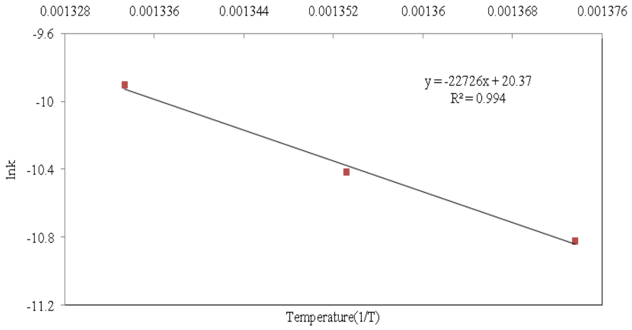


Figure 2
LnK as a Function of 1/T C$_{24}$

2.1.2 Overall Kinetic Parameters

The kinetic parameters for the overall pyrolysis reaction of HDPE were calculated using the semi batch reactor under isothermal conditions at three temperatures (477°C, 466°C and 455°C). In order to calculate the conversion, the ratio of the weight of collected oil/wax to the total weight of collected oil/wax was determined at each time. The method of calculation is the same method discussed earlier. Calculated overall activation energy and the pre exponential factor were 113.17 kJ/mol and 4.85E+5 (1/sec).

2.2 Non Isothermal Condition

Coast-Redfern method was applied for calculating the kinetic parameters under non isothermal conditions; this was also used by other researchers for the thermal degradation of plastic (Ballice, L., 2001; Fischer, P.E., Jou, C.S., & Gokalgandhi, S.S., 1987; Gao, Z., Amasaki, I., Kaneko, T., & Nakada, M., 2003a; Sinfronio, F.S.M., Santos, J.C.O., Pereira, L.G., Souza, A.G., Conceicao, M.M., Fernandes Jr, V.J. et al., 2005). The oil/wax fraction was analysed using GC/FID (shimadzu 17A) to calculate the kinetic parameters by applying the integral method discussed below. By substation of Arrhenius Equation (7) in the first order reaction rate, Equation (4), the following Equation (8) is obtained.

$$\frac{dx}{dt} = k_o\, e^{-\frac{E_a}{RT}} (1-x) \tag{8}$$

By integrating Equation (8) and substituting the constant heating rate a=dT/dt, Equation 8 results in the following expression:

$$\int_0^x \frac{dx}{1-x} = \frac{k_o}{a}\int_{T_0}^{T} e^{-\frac{E_a}{RT}} dT \tag{9}$$

Assuming that E$_a$/2T»1, which is always true, the temperature integral can be approximated by Equation 10 (Sinfronio, F.S.M. et al., 2005).

$$\int_{T_0}^{T} e^{-\frac{E_a}{RT}} d_T \approx \frac{R}{E_a} T^2 e^{-\frac{E_a}{RT}} \Big]_{T_0}^{T} \tag{10}$$

The replacement of applied approximation on Equation 9 yields Equation 11.

$$-\ln(1-x) = \left(\frac{RK_o}{aE_a}\right) T^2 e^{-\frac{E_a}{RT}} \Big]_{T_0}^{T} \tag{11}$$

For a reasonable temperature difference, the right–hand side with the lower limit can be ignored as it will be small. By re-arranging, then taking a natural logarithm, Equation 12 is obtained.

$$\ln\left(\frac{-\ln(1-x)}{T^2}\right) = \ln\frac{K_oR}{aE_a} - \frac{E}{RT} \tag{12}$$

Where Ea is the activation energy (J/mol), R is the universal gas constant (8.314 J/mol.K), and K$_o$ is the pre-exponential factor (1/sec). The plot of ln $\left(\frac{-\ln(1-x)}{T^2}\right)$ versus 1/T leads to a straight line with slope of –E$_a$/R and intercept of ln$\left[\frac{K_oR}{aE_a}\right]$. Activation energy is calculated from the slope of Equation 12 and the pre-exponential factor is determined from the values of the intercept and known activation energy. Table 2 shows the overall kinetic parameters at different temperatures between 455°C and 495°C. The results reveal that activation energy has a 20 percent variation within the studied temperature range. Results indicate a 20% increase in the activation energy on pyrolysis when the temperature decreases from 495 °C to 455 °C.

Table 2
Kinetic Parameters of HDPE (Pellet) under Non Isothermal Condition Using a Semi Batch Reactor

Temperature (°C)	Activationenergy (kJ/mol)	Pre-exponential factor (1/sec)
495	65.33	2.25E+04
477	65.04	2.48E+04
466	68.13	1.15E+06
455	82.29	4.57E+05

3. KINETIC STUDY USING TGA UNDER NON ISOTHERMAL CONDITIONS

The kinetic analysis described in the previous section was based on the measurements obtained from the semi batch reactor under isothermal and non isothermal conditions. In the following section kinetic analysis is based on pyrolysis conducted for small size samples using TGA under non isothermal conditions with different heating rates. Conversion (x) is defined by the following Equation-assuming no left residue:

$$x = \frac{M - m_t}{M} \tag{13}$$

Where M is the initial weight of the sample and m_t is the weight of the sample at time t. The kinetic parameters were calculated based on Equation 12.

3.1 Effect of Heating Rate

According to Figure 3, the weight loss curve has been shifted to the higher temperatures when the heating rate is increased. At a high heating rate significant temperature distribution will occur in the sample, leading to a surface sample temperature measured by TGA as being much higher than the bulk temperature.

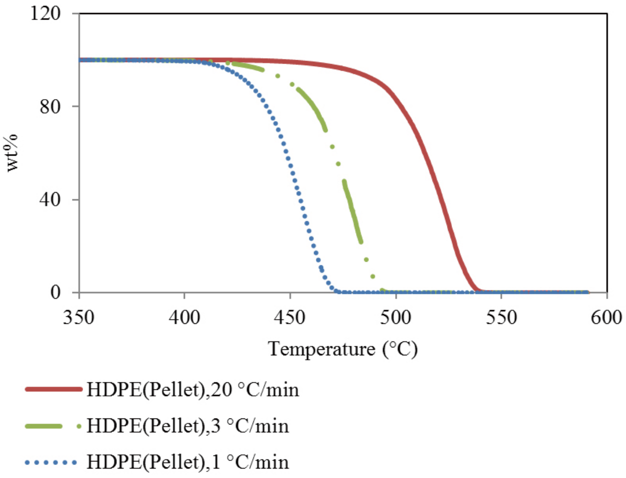


Figure 3
Weight Loss Vesus Temperature Profile at Different Heating Rate 1, 3, 20° C/min, Temperature of 590°C and 50ml/min N_2 Flow Rate Using HDPE (Pellet)

Figure 3 shows that the pyrolysis reaction starts at a measured temperature of 345°C, 402°C and 440°C at a heating rate of 1°C/min, 3°C /min and 20°C/min. The reaction is almost complete (99% conversion) at 429°C, 483°C and 525°C. The same trend for HDPE (Ballice, L., 2001; Encinar, J.M. &Gonzalez, J.F., 2008; Kayacan, I. &Dogan, O.M., 2008; Ranzi, E. et al., 1997; Sinfronio, F.S.M. et al., 2005) was observed by other researchers. In this study, the activation energy values of HDPE have been calculated between 95.64-274.72 kJ/mol for heating rates between 1°C/min to 20°C/min and different N_2 flow rates (see Table 3).

Table 3
Overall Kinetic Parameters under non Isothermal Condition Using TGA

	Activation Energy (kJ/mol)		
Heating Rate	N_2 Flow Rate (ml/min)		
(°C/min)	20	50	100
1	95.64	110.63	131.53
3	121.65	198.86	218.59
20	201.92	263.40	274.72
	Pre-exponential Factor (1/sec)		
1	3.99E+06	4.55E+07	1.36E+09
3	2.99E+08	7.297E+13	1.38E+15
20	3.23E+13	5.356E+17	2.51E+18

Reported values in literature are 268 kJ/mol(Bockhorn, H. et al., 1999b), 396-493 kJ/mol (Kayacan, I. &Dogan, O.M., 2008), 146.5 kJ/mol (Khalturinskii, N.A., 1987), 126-275kJ/mol (Sinfronio, F.S.M. et al., 2005), 243.8kJ/mol (Encinar, J.M. &Gonzalez, J.F., 2008), 238.4 kJ/mol (Ballice, L., 2001), and 233.2kJ/mol (Wu, C.H., Chang, C.Y., Hor, J.L., Shih, S.M., Chen, L.W., & Chang, F.W., 1993). The details of the literature data are tabulated in Table 4. Reported results in this study are in agreement with the literature. It is worth noting here that the effect of the heating rate on activation energy as obtained from TGA measurement is rather misleading. The true activation energy should not change with heating rate or temperature. The effect seen in Table 3 and in all the works reported in the literature is due to the nature of thermal treatment in TGA. The thermal conductivity of the plastic is very low and hence the temperaure distribution in the sample will be significant at a high heating rate. The effects of the heat transmission on kinetic studies were mentioned in a few studies (Bockhorn, H. et al., 1999b; Ceamanos, J. et al., 2002; Mastral, J.F. et al., 2007; Sinfronio, F.S.M. et al., 2005). For the heating rate of 20°C/min, Figure 3 shows that pyrolysis does not start until the temperature reaches 440°C, which is very unrealistic when compared to the results obtained in any pyrolysis reactor in which the pyrolysis starts at much lower temperature. This agrees with the results obtained at low heating rates.

Analysis using TGA should be extracted only from measurements conducted at a low heating rate and low N_2 flow rate. Similar observations has been reported for DSC analysis of low thermal conductivity materials (Albright, G., Farid, M., & Al-Hallaj, S., 2010). The reason for the wide discrepancy in the measured values of activation energy (apart from the characteristics of the sample) could be attributed to a defective heat transfer and a complex mechanism of decomposition due to diverse operating conditions in the literature.

Table 4
Kinetic Parameters for Pyrolysis of PE in Literature

Sample	Applied method	Initial sample mass (mg)	Temperature (°C)	Heating Rate (°C/min)	Nitrogen Flow Rate (mL/min)	E_a (kJ/mol) & K_o(1/sec)	Ref.
				Non Isothermal Condition			
HDPE	Coast-Redfern (Integral)	5	900	5/10/20	50	202/208/247 3.6E11/9E11/5.1E14	(Sinfronio, F.S.M. et al., 2005)
LDPE	Coast-Redfern (Integral)	5	900	5/10/20	50	126/212/235 1.6E6/2.8E12/8.5E13	(Sinfronio, F.S.M. et al., 2005)
LDPE	Differential	30	800	5/10/20/30/37	250	254/259/227/223/220 5.5E15/2.9E17/8.4E16/9.6E17/3.6E19	(Encinar, J.M. &Gonzalez, J.F., 2008)
HDPE	Combination of Coats-Redfern & Chen-Nuttall (Integral)	-	600	5/10/15	15	238 No record	(Ballice, L., 2001)
LDPE	Combination of Coats-Redfern & Chen-Nuttall (Integral)	-	600	5/10/15	15	209 No record	(Ballice, L., 2001)
HDPE	Ozawa-Flynn-Wall (Differential)	3	<430	5/12/25/50	80	273/171/164/163 5.6E16/1.5E9/6.7E8/8.4E8	(Ceamanos, J. et al., 2002)
HDPE	Ozawa-Flynn-Wall (Differential)	3	>430	5/12/25/50	80	376/373/363/344 3.2E24/1.9E24/3.4E23/2.5E22	(Ceamanos, J. et al., 2002)
HDPE	Integral	5-5.5	600	4/6/8/10/20	50	201 1.6E12	(Gao, Z. et al., 2003b)
				Isothermal Conditio			
LDPE	Differential	10-100	400-500	-	200-300	285 2.3E18	Isothermal Condition (Encinar, J.M. &Gonzalez, J.F., 2008)
HDPE	Ozawa-Flynn-Wall (Differential)	3	390/410/430/450/470	12	80	248 2.9E15	(Ceamanos, J. et al., 2002)
HDPE	Integral	5-5.5	440/450/460	20	50	194 9E11	(Gao, Z. et al., 2003b)
HDPE	Integral	40	430-480	-	25 (Helium)	268 5.2E7	(Bockhorn, H. et al., 1999b)

3.2 Effect of N_2 Flow Rate

The lower flow rate of N_2 prevents fast purging of the pyrolysed gaseous products and increases their residence time, which leads to a further cracking in the gas phase. Table 3 shows that the values of activation energy decreased as the N_2 flow rate decreased. Figure 4 shows the effect of using different N_2 flow rates on mass loss. The increase in N_2 flow rate increases the Biot Number of the sample, which leads to more temperature distribution in the sample and an external heat transfer that is much faster than the internal heat transfer. This suggests that the true activation energy should be obtained at a very low N_2 flow rate.

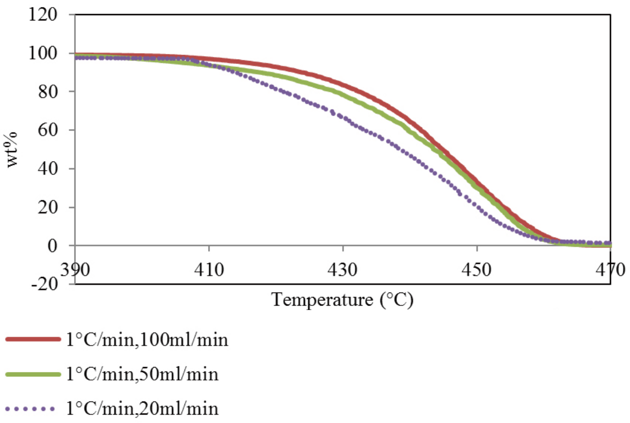


Figure 4.
Weight Loss Versus Temperature for N_2 Flow Rate of 100, 50, 20 ml/min, Heating Rate of 1°C/min, and Temperature of 590°C Using HDPE (Pellet)

3.3 Effect of Metal Particles in the Mixture with Plastic

The influence of metal on pyrolysis kinetics is verified in Figure 5. This Figure shows the effect of using powdered HDPE to improve the contact area in the TGA pan and using aluminum powder with the HDPE. The reduction in the apparent pyrolysis temperature when the HDPE is used in powder form is due to the improved heat transfer through the sample, which confirms the hypothesis outlined earlier. Calculated kinetic parameters reflect a significant lessening in the presence of metal (Table 5). Likewise, by reducing the physical dimensions of the plastic from pellet (3mm to 1mm) to powder form (less than 0.5 mm) a reduction of over 13 percent is seen in activation energy. In the literature, the effect of metals and catalysts on pyrolysis shows a similar fingerprint and lower activation energy. The effect of the catalyst (i.e. an ammonium-exchanged zeolite chabazite) was investigated in kinetic studies of polyethylene (Fernandes Jr, V.J., Araujo, A.S., Medeiros, R.A., Matos, J.R., Mercuri, L.P., Silva, A.O. et al., 1999). Reported activation energy was 29 percent less compared with the results without the catalyst. Moreover the onset temperature also decreases in the presence of a catalyst. Other researchers (Uemichi, Y., Makino, Y., & Kanazuka, T., 1989) have shown that impact of added metals on activated carbon in the degradation of polyethylene is that the total yield decreases.

Parameters such as the contact time and the type of the metal change the composition of the product. This effect reveals that metals play a catalytic role. Some researchers (Day, M., Cooney, J.D., & MacKinnon, M., 1995; Lee, J.Y., Liao, Y., Nagahata, R., & Horiuchi, S., 2006) have accepted the catalytic role of metal in the degradation of the plastic. In 1995, Day et. al. applied polypropylene and polyvinyl chloride in the presence of copper, iron oxide, and dirt. Their results confirmed that in the presence of 5 percent copper, the degradation process was accelerated by 100 percent, the onset temperature was lowered, (26.2°C reduction at 5°C/min heating rate) and there were significant differences in activation energy (around 20 percent lower). Similar results (Lee, J.Y. et al., 2006) were obtained by incorporating Palladium nano-particles in polymer films (polystyrene and polypropylene), verifying the ability of metal particles to suppress the chain transfer reaction. The calculated activation energy for the pyrolysis of scrap printed circuit board plastic (Guo, Q., Yue, X., Wang, M., & Liu, Y.), which is a mixture of metal and plastic, were 90.488 kJ/mol and 137.796 kJ/mol in the temperature range of 280°C-333 °C and 330°C-390°C respectively. The results reported in this paper indicate that the effect of metal is in accelerating pyrolysis reaction in thermal and not catalysis; what is reported in the literature. This is in agreement with the results reported in the literature using DSC measurements conducted for low thermal conductivity materials(Albright, G. et al., 2010).

Table 5
Activation Energy for HDPE (Pellet) and HDPE (Powder) with and without Al (Powder)

Sample	E_a (kJ/mol)	Pre-exponential factor (1/sec)
HDPE (pellet)	239.99	4.09E+15
HDPE (powder)	206.84	1.21E+14
HDPE (powder)+Al	52.84	4.36E+02

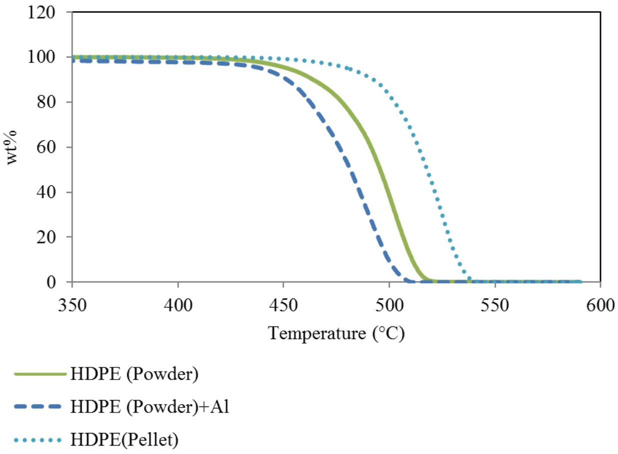


Figure 5
Weight Loss Versus Temperature at Different Physical Appearance Using HDPE (Pellet) and HDPE (Powder) with Al (Powder) at Heating Rate of 20°C/min, Temperature of 590 °C, and N_2 Flow Rate of 150ml/min

CONCLUSIONS

The kinetic parameters of HDPE pyrolysis under non isothermal conditions using TGA and isothermal and non isothermal conditions using a semi batch reactor were determined. An analysis of non isothermal data was obtained using the Coats-Redfern method and assuming a first order reaction rate. The analysis of TGA results show that activation energies increase with the heating rate in all applied N_2 flow rates, due to heat transfer limitations. Hence, kinetics analysis using TGA should be extracted only from measurements conducted at low heating rates with a low N_2 flow rate. The activation energy 95.64 (kJ/mol) and pre exponential factor 3.99E+6 (1/sec) are calculated kinetic values at 1°C/min and 20 (ml/min) under non isothermal conditions. The highest and lowest values of activation energy, 116.68 and 226.96 kJ/mol respectively, were calculated for C_{14} and C_{30} and the overall activation energy of 113.17 kJ/mol was calculated using a semi batch reactor under isothermal condition. Lower overall activation energies (between 65.04-82.29 kJ/mol) were calculated under non isothermal conditions using a semi batch reactor. This is believed to be due to heat transfer limitations.

The wide discrepancy in the activation energy values obtained could be attributed to defective heat transfer and a complex mechanism of decomposition, due to diverse operating conditions in the literature. The presence of metal particles in the plastic mixture accelerated the rate of reaction very quickly, which is more likely due to heat transfer enhancement.

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