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Kinetics of Thermal Pyrolysis of High-Density Polyethylene

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Abstract

Thermal pyrolysis kinetics of virgin high-density polyethylene (HDPE) was investigated. Thermal pyrolysis of HDPE was performed using a thermogravimetric analyzer in nitrogen atmosphere under non-isothermal conditions at different heating rates 4, 7, 10 °C/min. First-order decomposition reaction was assumed, and for the kinetic analysis Kissinger-Akahira-Sunose(KAS), Flynn-Wall-Ozawa(FWO) and Coats and Redfern(CR) method were used. The obtained values of average activation energy by the KAS and FWO methods were equal to137.43 and 141.52 kJ/mol respectively, these values were considered in good agreement, where the average activation energy value obtained by CR equation methods was slightly different which equal to 153.16 kJ/mol.

Keywords: Thermogravimetric, Kinetic, Thermal degradation, Polyethylene

1- Introduction

Production of plastic has increased by an average of 10% every year on a global basis since 1950[1,2]. On other hand the duration life of plastic is very small.

Almost 40% of plastic consumed has duration of life smaller than one month. The service life of plastic products ranges from 1 to 35 years depending on the area of application [3]. So the increase in plastic wastes because of the frequent use of such materials was expected result.

At the same time, not all of these materials were recycled or treated therefore the disposal of these wastes has become a major environment concern [4].

As a conventional plastic material, polyethylene (PE), with its two types; high density polyethylene (HDPE) and low density polyethylene (LDPE) [5], continues to play an essential part in the commodities because of its resistance to microbial or enzymatic degradation. In addition is a major component of plastic waste from domestic refuse [6]. Also polyethylene it is one-third of the global consumption of plastic [3].

The plastic wastes accumulation problems took a lot of attention because of the importance of the issue. Many of the solutions presented one of them is the landfilling of plastic wastes but this is unhelpful method due to slow degradation rates of plastic (10 to 450 years), soil pollution by plastic additives, polluting ground water and decreasing the landfill region [1,4].

Another solution is by using incineration method but it is costing and it has caused environmental problems since it generates several pollutants to the atmosphere. So to reduce the damages and environmental impact caused by plastic wastes materials, they must be recycled and recovered [7].

Recycling is able to solve the problem of waste plastic. It divided into two categories to mechanical recycling (primary and secondary) and feedstock recycling or chemical recycling [8]. This method involves different techniques, including pyrolysis, hydrolysis, methanolysis, hydrogenation, and gasification [1].

Pyrolysis method is the most beneficial among the chemical recycling methods [1]. Pyrolysis is thermochemical decomposition of organic materials in the absence of oxygen. It can be carried out in the absence of catalyst which is called thermal cracking or thermolysis and catalytic pyrolysis in the presence of a catalyst [9].

Pyrolysis has become very promising technology for treating the waste plastic since plastics have a high calorific value of more than 40 MJ/kg which is similar to those of common liquid fuels such as kerosene, gasoline, diesel, etc. [7].

The pyrolysis products include a carbonized char (solid residues) and a volatile fraction. A portion of the volatile fraction can be condensed to give olefins, paraffins, isoparaffins, naphthenics, and aromatics, while the remaining is a non-condensable high calorific value gas [10].

Thermal pyrolysis involves the degradation of the plastic materials by heating them to temperature between 350 to 900 °C in the absence of oxygen to make sure that no oxidation of the polymer takes place [9].

Thermogravimetric analysis (TGA) is the main gate to understand the pyrolysis. TGA is a technique of thermal analysis which measure the rate of change in the weight and the amount of material as a function of temperature or time under controlled atmosphere such as nitrogen, air, or other gases [11].

TGA is considered as an excellent mean for studying the kinetics of degradation [12].

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There are various methods to calculate the isothermal or non-isothermal solid-state kinetic data from TGA. In general the most common of them can be classified into two major types: model-fitting and model-free methods that are listed in Table 1 [10, 13].

Table 1. Non-isothermal Methods for studying solid-state kinetics [10,13]

Model-fitting	Model-free
• Differential	• Kissinger
• Freeman-Carroll	• Flynn-Wall and Ozawa
• Coats and Redfern	• Vyazovkin and AIC
	• Kissinger-Akahira-Sonuse

In the model-fitting method, different reaction models are fitted to the experimental data then the best model selected when giving the best statistical fit from which the activation energy (E_a) and frequency factor (A) are calculated. However, model-fitting methods were broadly applied due to their ability to calculate the kinetic parameters directly from the results of TGA [13,14].

Model-free methods or iso-conversional methods estimate the activation energy at specific extent of conversion without the need for assumed reaction model [15]. Sometimes it is called multi-curve methods because these methods require more than one kinetic curve to perform the analysis and these methods need different heating rates to calculate the activation energy [14].

Many researchers study the decomposition of different materials by applied the models of TGA such as degradation of polycarbonate [16], degradation of synthesized optically active polyamides[17], decomposition of Huadian oil shale [18], thermal decomposition of tea waste [19], pyrolysis and gasification kinetics of the two tropical biomass species[20], thermal stability behavior of coconut coir, banana pseudo stem, pineapple leaf, and sugarcane bagasse fibers [21].

Shubbar [22] study the pyrolysis of LDPE and HDPE in closed system batch reactor and obtained the temperature range, from TGA, for LDPE from 380 to 507°C, while, the temperature range for HDPE was found from 386.5 to 514°C.

Kayacan et al. [23] study the thermal decomposition kinetics of LDPE and HDPE at 5, 10, 20 and 50 K/min heating rates it was found that the kinetics of the degradation of the LDPE and HDPE for non-isothermal conditions can be considered as a first-order reaction and the activation energy for raw HDPE has been calculated between 401 and 470 kJ/mol and for the waste HDPE was in the range of 396 to 493 kJ/mol. The activation energy values have been found for raw LDPE between 324 and 497 kJ/mol and 271 to 333 kJ/mol for the waste LDPE.

Kumar et al. [1] study the TGA has been used for the non-isothermal kinetic study of waste high-density polyethylene pyrolysis under nitrogen atmosphere at different heating rates 10, 20 and 40 °C/min.

The activation energy values of waste HDPE have been calculated as 207.43, 268.22 and 473.05 kJ/mol at 10, 20 and 40 °C/min heating respectively.

Abbas and Mohamed [24][25] reported TGA for high-density polyethylene (HDPE) and low density polyethylene (LDPE) at the heating rate equal to 20 °C/min from surrounding temperature to 800 °C in order to know the range of effective temperature for pyrolysis.

The decomposition of LDPE started at 349 °C and completed at 489 °C, whereas the HDPE decomposition started at 326 °C and completed at 495 °C.

In the present work, the kinetics of the thermal degradation using TGA of virgin HDPE was studied according to different models methods; Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Coats and Redfern (CR). The values of activation energy for waste HDPE have been obtained in non-isothermal condition assuming firstorder reaction kinetic at different heating rates.

2- Experimental

2.1. TGA procedure

The thermal decomposition behavior was studied by TGA analyzer apparatus (type LINSEIS STA PT-1000 TGA) which shown in figure 1. Twenty milligrams of the virgin HDPE were placed on the sample holder and pyrolyzed in nitrogen atmosphere in each experiment.

Pyrolysis was carried out at non-isothermal conditions with temperature range from room temperature to about 600 °C and the TGA and differential gravimetric analysis (DTGA) data were recorded at different heating rate (H_r) (4, 7 and 10 °C/min.). The main physical properties of virgin HDPE pellets are shown in table 2.

Fig. 1. Thermogravimetric TGA analyzer

Table 2. Virgin HDPE pellets physical properties

Property	Value
Average particle diameter, mm	3
Density, g/cm^3	0.956 - 0.963
Deflection temperature (at 0.46 Mpa), °C	75 – 85
Melting point, °C	130 – 135
Melt flow index, g/10min	0.05 - 0.43

2.2. Non-Isothermal Kinetic Study Using TGA

The non-isothermal kinetics for pyrolysis is usually written as follows:

$$\frac{dX}{dt} = Kf(X) \tag{1}$$

Where X is a conversion of HDPE, and is given by:

$$X = \frac{Wi-W}{Wi-Wf} \tag{2}$$

Where W, W_i, and W_f, represent the instantaneous, initial, and final weights of the sample. The reaction rate constant k is expressed in terms of the Arrhenius equation as:

$$k = A\,exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

And the function f(X) can be written as:

$$f(x) = (1-X)^n \tag{4}$$

Substituting Eq. (3) and (4) into Eq. (1) gives:

$$\frac{dX}{dt} = A\,exp\left(-\frac{E_a}{RT}\right)(1-X)^n \tag{5}$$

For a constant heating rate H_r=dT/dt, Eq. (5) can be rearranged to the following equation:

$$\frac{dX}{dT} = \left(\frac{1}{H_r}\right)A\,exp\left(-\frac{E_a}{RT}\right)(1-X)^n \tag{6}$$

Equation (6) represents the differential form of the non-isothermal rate law [14][26].

The thermal analysis methods start from the general differential kinetic Eqs. (5) and (6) or the integral forms of them as follow.

a. The KAS Method

The KAS method was based on the following equation:

$$\ln\left(\frac{H_r}{T^2}\right) = \ln\left(\frac{AR}{E_a g(x)}\right) - \frac{E_a}{RT} \tag{7}$$

Where g(x) is the integral conversion function (reaction model) which is reported in the literature [27]. For constant conversion a plot of left side of the above equation against 1000/T at different heating rates is a straight line whose slope and intercept can evaluate the activation energy and pre-exponential factor, respectively [28].

b. The FWO Method

The FWO method is based on the following equation:

$$\ln(H_r) = \ln\left(\frac{AE_a}{Rg(x)}\right) - 5.331 - 1.052\frac{E_a}{RT} \tag{8}$$

Thus, for a constant conversion, a plot of natural logarithm of heating rates, ln(H_r),versus 1000/T obtained from thermal curves recorded at different heating rates will be a straight line whose slope (−1.052(Ea/R)) from which the activation energy can be determined [14].

c. The CR method

Taking the logarithm of both sides of Eq. (6) gives:

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\frac{AR}{H_rE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{RT} \tag{9}$$

If n=1

$$\ln\left[\frac{-\ln(1-X)^{1-n}}{(1-n)T^2}\right] = \ln\frac{AR}{H_rE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{RT}\ \text{if}\ n\neq 1 \tag{10}$$

The above two Equations (9 and 10) are the CR method the plot of left hand side of the above equations (9 and 10) on ($\ln[-\ln(1-X)/T^2]$) the y-axis versus 1/T. Accordingly, the apparent activation energy (E_a) and the apparent frequency factor (A) can be determined from the slope and intercept of the regression line, respectively [29,30].

3- Results and Discussion

3.1. TGA and DTGA of HDPE

The thermal stability of the polymeric materials plays a crucial role in determining the limit of their working temperature and the environmental conditions for uses, which are related to their thermal decomposition temperature and decomposition rate. TGA applied in determination of the study of thermal stability/degradation of waste HDPE in various ranges of temperature [1].

The TGA and DTGA curves of the pyrolysis of HDPE under nitrogen atmosphere obtained at three different heating rates of 4, 7 and 10 °C/min are shown in figures 2 and 3.

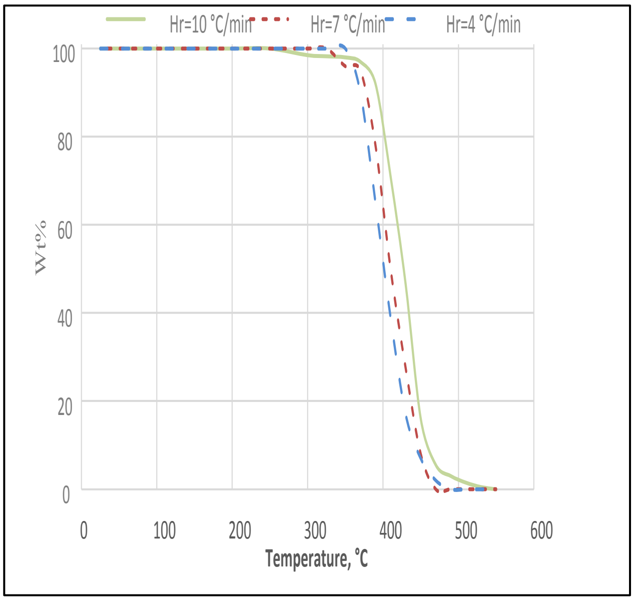

Fig. 2. TGA of virgin HDPE at different heating rates

In the figure (2) curve the initial temperature at which the degradation started and final temperature at which the degradation completed for waste HDPE was 370.2 and 492.8°C, 370.9 and 463.9 °C, 381 and 510 °C at the heating rates of 4, 7 and 10 °C/min, respectively. These results are in good agreement with recorded degradation temperature ranges for HDPE by AL Mustapha and Andresen and by used A Pyris 1 Thermal Gravimetric analyzer (TGA1), at a heating rate of 10 °C/min from 35 to 900 °C in a nitrogen gas atmosphere with a flow rate of 20 ml/min [26], also ABOULKAS and HARFI recorded that by used the Rheometrix Scientific STA 1500 TGA analyzer at four different heating rates (2, 10, 20 and 50 K/min) between 300 K and 1273 K [28].

The rate of mass loss is temperature dependent: the higher the temperature, the larger the mass loss [14]due to the fact that polymer molecules does not have enough time to exhaust the heat with increasing heating rate, leading to slower decomposition rate [1].

It is clearly in figure (2) that there is a shift in the weight loss data to higher temperatures as the heating rate increases, because the rate of heat transfer at various heating rates is different, and the exposure time at the higher heating rate is shorter, as well as the effect of the kinetics of decomposition [18]. The same behavior was realized by several previous works [31][1].

DTGA curves for waste HDPE at 4, 7 and 10 °C/min heating rates (Figure 3) contains one peak this indicates that there is one degradation step at different heating rates[1].

The maximum degradation temperature (T_{max}) of HDPE takes place at 450, 410 and 405 °C at 10, 7 and 4 °C/min heating rates respectively as shown in figure 3. The recorded values of T_{max} for HDPE are in the range between 461 and 493 °C at H_r equal to 10 °C/min [1,31,32].

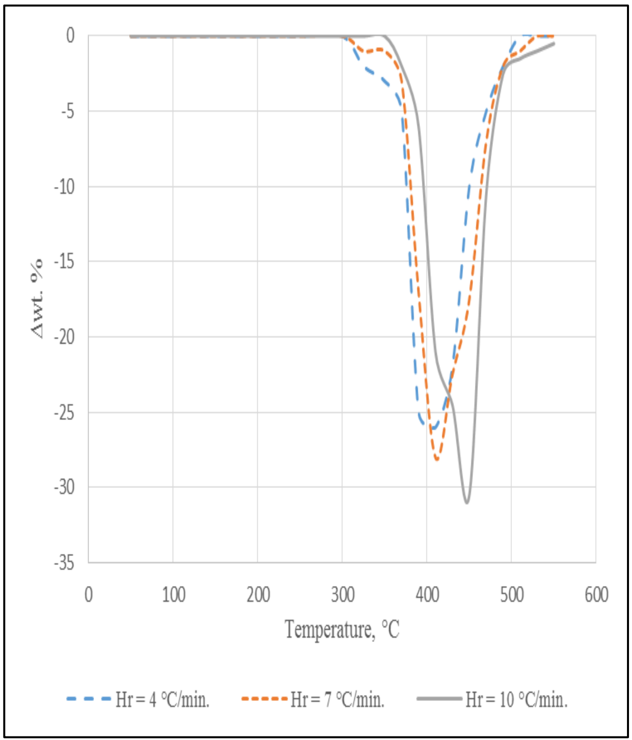

Fig. 3. DTGA of virgin HDPE at different heating rates

3.2. Conversion of HDPE and TGA kinetics analysis

The conversion versus TGA temperature of HDPE at different heating rates is shown in figure 4. The conversion of HDPE increased with temperature at different heating rates. At 10, 7 and 4 °C/min the conversion increased from 8, 22, and 35 % at 390 °C respectively to 100% at 550 °C for all heating rate.

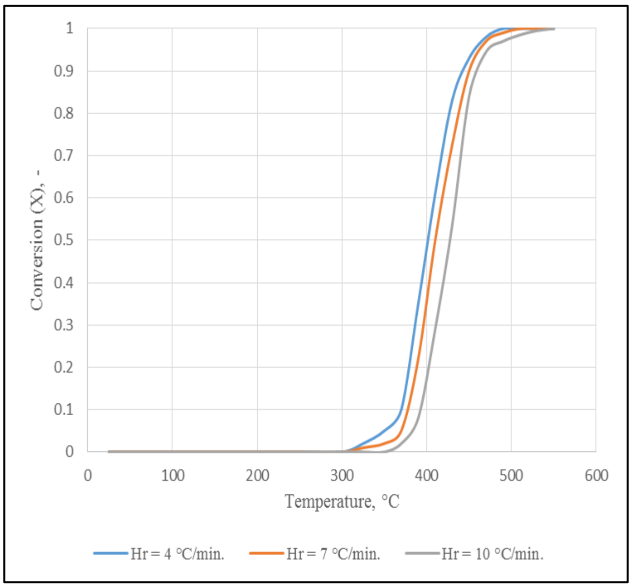

Fig. 4. Conversion of virgin HDPE versus TGA temperature at different heating rates

The results obtained from TGA were analyzed according to KAS, FWO and CR methods to calculate the activation energy (E_a) and pre-exponential factor (A).

The kinetic parameters obtained by KAS and FWO methods were calculated according to equations (7) and (8), respectively. The activation energy and preexponential factor were calculated as a function of conversion by using iso-conversional methods of KAS and FWO methods for the range of conversion from 0.05 to 0.95 is considered for calculating the kinetic parameters by these methods.

The iso-conversional plots of these methods are shown in figures 5 and 6 respectively.

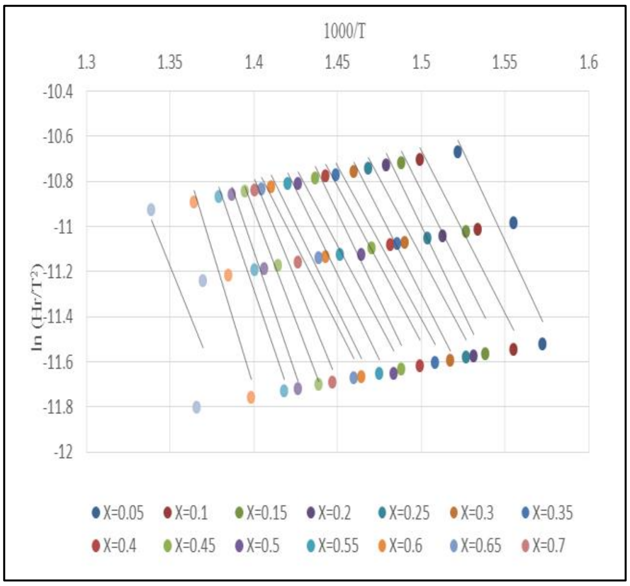

Fig. 5. KAS plots of HDPE at different values of conversion.

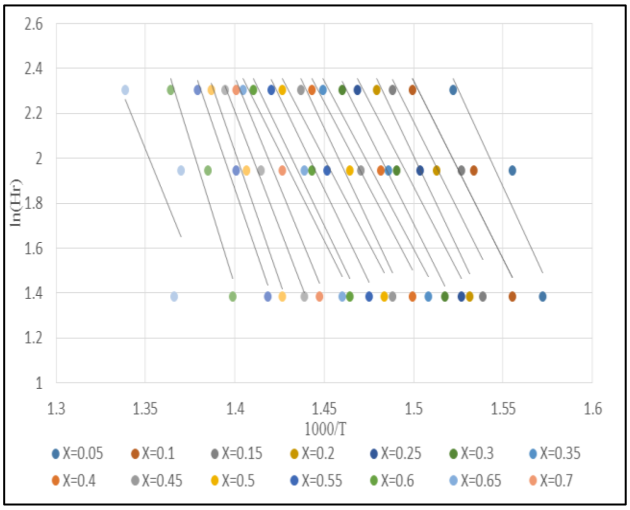

Fig. 6. FWO plots of HDPE at different values of conversion

Figure (7) was show that the activation energy depends upon extent of conversion for both KAS and FWO methods. In general, the calculated values of activation energy by FWO were slightly higher but in the same order of magnitude for those calculated by KAS.

At the beginning of reaction, the activation energy values have oscillated in the same scale of about 120 and 136 kJ/mole. After 65 % of HDPE converted the activation energy values rise to its higher values (203 to 204 kJ/mol for KAS and FWO, respectively). At 90% of HDPE conversion, the activation energy then lowering near the end of reaction to about 151 to 155 kJ/mol for KAS and FWO, correspondingly.

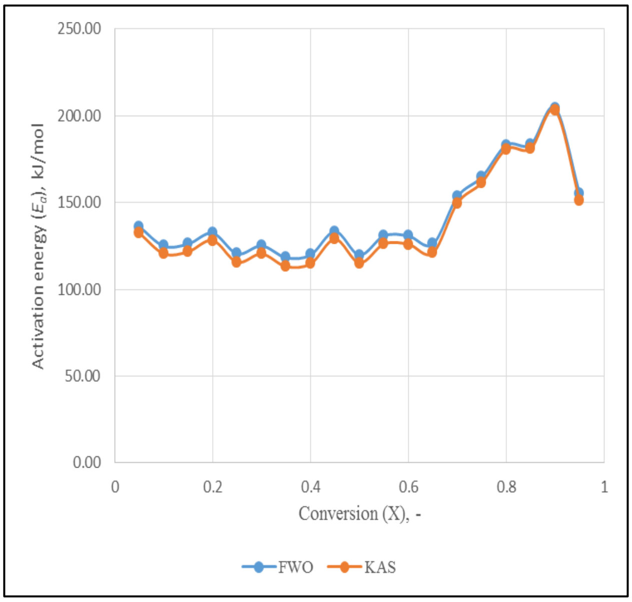

Fig. 7. The activation energy as a function of conversion using KAS and FWO technique

Figure 8 shows the plot of the CR method for waste HDPE under non-isothermal conditions. In this figure, as the entire range of $\ln(-\ln(1-x)/T^2)$ as a function of 1/T, the data could be represented by a single straight line for all three heating rates. Reasonable fits of data to straight lines indicate that the assumption of first-order kinetics for thermal decomposition of waste HDPE is acceptable. The activation energy and pre-exponential factor values are shown in table 3.

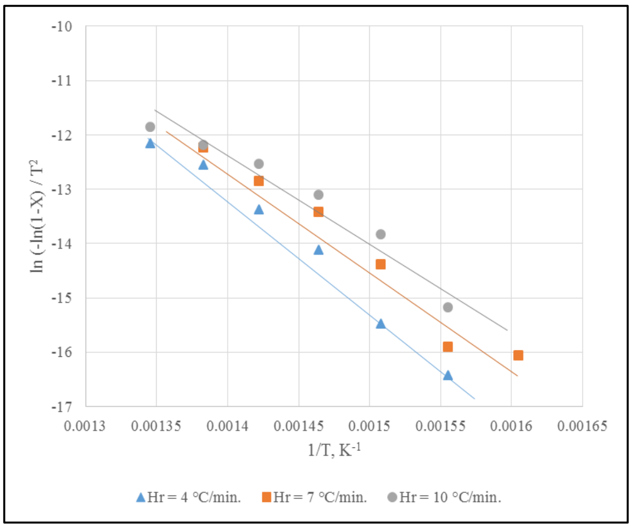

Fig. 8. CR method plots of HDPE at different values of conversion

Table 3. Calculated kinetic parameters for HDPE by CR method at different heating rate

H_r, °C/min	E_a, kJ/mol	A, min^{-1}
10	175.866	$3.35*10^{12}$
7	156.6191	$1.46*10^{11}$
4	126.9964	$4.83*10^{8}$

Activation energy increased with increase in heating rate due to very low thermal conductivity of polymeric material and hence the temperature maldistribution in the waste HDPE sample will be significant at a high heating rate [1] The average activation energy calculated by KAS, FWO and CR are137.43, 141.52 and153.16 kJ/mol respectively. These differences could be due to the approximations used for the temperature integral used in these methods [18,33], and are in good agreement with the reported activation energy[26,28,31,32].

4- Conclusion

The kinetic parameters of waste HDPE decomposition under non-isothermal conditions using TGA were determined. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum decomposition regimes.

The TGA experiment showed that the degradation temperatures for waste HDPE at which the maximum weight losses take place were about 389.4, 398.2 and 434.1 °C at the heating rates of 4, 7 and 10 °C/min, respectively. The main pyrolysis process occurred in the temperature range 350 to 510 °C.

The average activation energy values of waste HDPE have been calculated by KAS, FWO and CR method are 137.43, 141.52 and 153.16 kJ/mol respectively for first-order decomposition reaction model.

References

[1] S. Kumar and R. K. Singh, "Pyrolysis kinetics of waste high-density polyethylene using thermogravimetric analysis," *Int. J. ChemTech Res.*, vol. 6, no. 1, pp. 131– 137, 2014.

[2] 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.

[3] C. Cleetus, S. Thomas, and S. Varghese, "Synthesis of Petroleum-Based Fuel from Waste Plastics and Performance Analysis in a CI Engine," *J. Energy*, vol. 2013, pp. 1–10, 2013.

[4] M. F. Ali and M. S. Qureshi, "Catalyzed pyrolysis of plastics : A thermogravimetric study," vol. 5, no. 9, pp. 284–292, 2011.

[5] M. A. Ja, "Production of Liquid Fuels from Recycled Plastics using Acidic HNaY Catalysts," 2011.

[6] M. T. Taghizadeh, P. Seifi-aghjekohal, A. Bahadori, and B. Zeraatkar, "Thermal and catalytic degradation study of polyethylene and investigation the catalytic effect of X-Zeolite and Silica-Alumina on degradation kinetic," *J. Iran. Chem. Res.*, vol. 2, pp. 195–210, 2009.

[7] M. Syamsiro, W. Hu, S. Komoto, S. Cheng, P. Noviasri, P. Prawisudha, and K. Yoshikawa, "Co-Production of Liquid and Gaseous Fuels from Polyethylene and Polystyrene in a Continuous Sequential Pyrolysis and Catalytic Reforming System," *Energy Environ. Res.*, vol. 3, no. 2, pp. 90–106, 2013.

[8] K. Lee, "Pyrolysis of Waste Polystyrene and High-Density Polyethylene," *Www.Intechopen.Com*, 2011.

[9] E. Apaydin-varol, S. Polat, and A. E. Putun, "PYROLYSIS KINETICS AND THERMAL DECOMPOSITION BEHAVIOR OF POLYCARBONATE – a TGA-FTIR study," vol. 18, no. 3, pp. 833–842, 2014.

[10] P. V Thorat, S. Warulkar, and H. Sathone, "ISSN 2277 – 7164 Review Article Thermofuel – ' Pyrolysis of waste plastic to produce Liquid Hydroocarbons ,'" vol. 3, no. 1, pp. 14–18, 2013.

[11] E. Rostek and K. Biernat, "Thermogravimetry as a Research Method in the Transformation Processes of Waste Rubber and Plastic Products for Energy Carriers (WtE and WtL Processes)," vol. 1, no. 2, pp. 163–171, 2013.

[12] X. G. Li, B. G. Ma, L. Xu, Z. T. Luo, and K. Wang, "Catalytic effect of metallic oxides on combustion behavior of high ash coal," *Energy and Fuels*, vol. 21, no. 5, pp. 2669–2672, 2007.

[13] N. Murichan and P. Cherntongchai, "Kinetic Analysis of Thermal Degradation of Polyolefin Mixtures," *Int. J. Chem. Eng. Appl.*, vol. 5, no. 2, pp. 169–175, 2014.

[14] M. Heydari, M. Rahman, and R. Gupta, "Kinetic Study and Thermal Decomposition Behavior of Lignite Coal," vol. 2015, 2015.

[15] K. Slopiecka, P. Bartocci, and F. Fantozzi, "Thermogravimetric analysis and Kinetic study of poplar wood pyrolysis," no. May, pp. 1687–1698, 2011.

[16] A. Marcilla, A. Gómez-Siurana, and D. Berenguer, "Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers," *Appl. Catal. A Gen.*, vol. 301, no. 2, pp. 222–231, 2006.

[17] S. Mallakpour and M. Taghavi, "The Accuracy of Approximation Equations in the Study of Thermal Decomposition Behaviour of Some Synthesized Optically Active Polyamides," *Iran. Polym. J.*, vol. 18, no. 11, pp. 857–872, 2009.

[18] X. Yongjiang, X. Huaqing, W. Hongyan, L. Zhiping, and F. Chaohe, "Kinetics of Isothermal and Non-Isothermal Pyrolysis of Oil Shale," *Oil Shale*, vol. 28, no. 3, p. 415, 2011.

[19] S. Polat, E. Apaydın, and A. E. Pütün, “TGA-FTIR study on the thermal decomposition of tea waste,” 2013.

[20] K. Oluoti, T. Richards, T. R. K. Doddapaneni, and D. Kanagasabapathi, “Evaluation of the Pyrolysis and Gasification Kinetics of Tropical Wood Biomass,” *BioResources*, vol. 9, no. 2, pp. 2179–2190, 2014.

[21] M. S. Alwani, H. P. S. Abdul Khalil, O. Sulaiman, M. N. Islam, and R. Dungani, “An approach to using agricultural waste fibres in biocomposites application: Thermogravimetric analysis and activation energy study,” *BioResources*, vol. 9, no. 1, pp. 218–230, 2014.

[22] A. S. Abbas and S. D. a Shubar, “Pyrolysis of High-density Polyethylene for the Production of Fuel-like Liquid Hydrocarbon,” *Iraqi J. Chem. Pet. Eng.*, vol. 9, no. 1, pp. 23–29, 2008.

[23] I. Kayacan, “Pyrolysis of Low and High Density Polyethylene . Part I : Nonisothermal Pyrolysis Kinetics,” pp. 385–391, 2008.

[24] F. A. M. Ammar S. Abbas, “Production and Evaluation of Liquid Hydrocarbon Fuel from Thermal Pyrolysis of Virgin Polyethylene Plastics,” *Iraqi J. Chem. Pet. Eng.*, vol. 16, no. MARCH, 2015.

[25] A. S. Abbas and F. A. Mohamed, “Kinetic Study of Hydrocarbon Liquid Production via Thermal and Catalytic Pyrolysis for Low-density Polyethylene,” *Diyala J. Eng. Sci.*, vol. 08, no. January, pp. 819–834, 2016.

[26] M. N. Almustapha and J. M. Andrésen, “Recovery of Valuable Chemicals from High Density Polyethylene (HDPE) Polymer : a Catalytic Approach for Plastic Waste Recycling,” *Int. J. Environ. Sci. Dev.*, vol. 3, no. 3, 2012.

[27] S. S. Idris, N. A. Rahman, K. Ismail, A. B. Alias, Z. A. Rashid, and M. J. Aris, “Bioresource Technology Investigation on thermochemical behaviour of low rank Malaysian coal , oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA),” *Bioresour. Technol.*, vol. 101, no. 12, pp. 4584–4592, 2010.

[28] A. Aboulkas and K. El Harfi, “Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen,” *Oil Shale*, vol. 25, no. 4, pp. 426–443, 2008.

[29] K. M. Lu, W. J. Lee, W. H. Chen, and T. C. Lin, “Thermogravimetric analysis and kinetics of co-pyrolysis of raw/torrefied wood and coal blends,” *Appl. Energy*, vol. 105, pp. 57–65, 2013.

[30] E. Sima-Ella, G. Yuan, and T. Mays, “A simple kinetic analysis to determine the intrinsic reactivity of coal chars,” *Fuel*, vol. 84, no. 14–15, pp. 1920–1925, 2005.

[31] S. C. O. Hee Taik Kim, “Kinetics of Thermal Degradation of Waste Polypropylene and Polyethylene,” *J. Ind. Eng. Chem.*, vol. 11, pp. 648–656, 2005.

[32] Ush, S. Salman, Jiri Mojtaba, and P. Mohammad, “Thermal degradation mechanism of HDPE Nanocomposites containing Nano,” vol. 3, no. 6, pp. 15–28, 2014.

[33] N. Sbirrazzuoli, L. Vincent, A. Mija, and N. Guigo, “Chemometrics and Intelligent Laboratory Systems Integral , differential and advanced isoconversional methods Complex mechanisms and isothermal predicted conversion – time curves,” *Chemom. Intell. Lab. Syst.*, vol. 96, no. 2, pp. 219–226, 2009.