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Thermal and Catalytic Degradation Kinetics of High-Density Polyethylene Over NaX Nano-Zeolite

Ammar S. Abbas* and Marwa G. Saber
Chemical Engineering Department – College of Engineering – University of Baghdad (Iraq)
*Email: dr_ammar19@yahoo.com, ammarabbas@coeng.uobaghdad.edu.iq

Abstract

Thermal and catalytic pyrolysis of waste plastics in an inert atmosphere has been regarded as a creative method, since pyrolysis can convert plastics waste into hydrocarbons that can be used either as fuels or as a source of chemicals.

Natural Iraqi kaolin clay was used to synthesis the NaX nano- zeolite by hydrothermal conditions with average particle size equal to 77.63nm.Thermal decomposition kinetics of high-density polyethylene (HDPE) in the absence and presence of catalysts nano NaX Zeolite was investigated. Thermal and catalytic degradation of HDPE was performed using a thermogravimetric analyzer in nitrogen atmosphere under non-isothermal conditions 4, 7 and 10 °C/min heating rates were employed in thermogravimetric analysis (TGA) experiments.

First-order decomposition reaction was assumed, and for the kinetic analysis Coats and Redfern (CR) method was used. The apparent activation energy (Ea) was evaluated. Results showed that the NaX nano-zeolite decreases the activation energy (Ea) of HDPE pyrolysis further than the thermal pyrolysis.

Keywords: Thermal degradation, HDPE, NaX Zeolite, TGA, Coats and Redfern, kinetic analysis.

Introduction

The good properties of plastics materials such as light weight, strength and energy efficiency make plastics a necessary part of many industrial applications. Annual plastic consumption of the world's increased dramatically. Thus, wastes of plastic are increasing rapidly which consider one of the big environmental problems [1]. As a conventional plastic material, polyethylene, with its two types HDPE and low density polyethylene [2], plays an important part in the commodities due to its resistance to microbial or enzymatic degradation also it is a main component of plastic waste from domestic waste [3]. Similarly polyethylene is one-third of the global consumption of plastic [4].

Several approaches, such as land filling, incineration, biological are already in place, but still appear insufficient or do not conform existing environmental rules [1].Thus, alternate methods such as chemical or feedstock recycling which includes conversion of plastics into fuel plays an important process in reducing plastics waste at the same time produce fuel[5] [6].

Pyrolysis is thermochemical decomposition of organic materials in the absence of oxygen [7]. 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 [4].

The disadvantages of thermal degradation are wide product distribution and requisite of high temperatures, usually more than 500 °C and even up to 900 °C. Catalytic degradation of plastics waste offers substantial advantages. On the other hand catalytic pyrolysis gives a means to solve the thermal pyrolysis problems [8].

Different catalysts have been used such as silica alumina catalyst [9], Fluid Catalytic Cracking (FCC) catalyst [10] [11], MCM-41[12], molecular sieves and Y zeolite [13], other zeolites such as beta zeolite [14], clinoptilolite[15], bentonite [16], zeolite-X [17] or ZSM-5 [18], have also been employed for the catalytic decomposition of plastic waste [19].

Zeolites materials have excellent properties as catalysts for the plastics pyrolysis waste [20]. The zeolite catalyst combines high acidity with shape selectivity, high surface area and high thermal stability [21]. In addition the Nano-sized zeolites have more active sites in catalysis compared with conventional zeolites caused by their larger external surface area [22].

Thermogravimetric analysis (TGA) consider an excellent mean for studying the kinetics of thermal and catalytic pyrolysis [23], by TGA the kinetic parameter of pyrolysis which include the activation energy (E_a) and pre-exponential (A) can be calculated. TGA is a technique of thermal analysis which measures 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 [24].

Abbas and Shubar [25]study the HDPE pyrolysis in closed system batch reactor and used the TGA to found the temperature range of HDPE pyrolysis, it was from 386.5 to 514 °C.

Kayacan et al. [26] study the waste and raw HDPE thermal decomposition kinetics at 5, 10, 20 and 50 K/min heating rates it was found that the kinetics of the degradation of the 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.

Kumar et al. [27] study the TGA has been used for the non-isothermal kinetic study of waste HDPE 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.

Abbas and Mohamed reported TGA for HDPE at 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 the HDPE decomposition started at 326 °C and was complete at 495 °C [28].

In the present work, nano NaX zeolite was prepared and the kinetics of the thermal degradation and catalytic in presence of nano NaX zeolite degradation using TGA of virgin HDPE was studied according to CR method. The values of activation for waste HDPE have been obtained in non-isothermal condition assuming first-order reaction kinetic at different heating rates.

Material and Methods

Materials

Natural Iraqi kaolin clay, sodium hydroxide (NaOH) and HDPE pellets were purchased from local markets (the source of plastic is SABIC Company). The main properties of the HDPE are shown in Table1.

Table 1: 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

NaX Zeolite Preparation

Kaolin was sieved to a particle size ≤ 75 µm, then mixed with 40% sodium hydroxide solution using (kaolin / NaOH = 1/1.5) and fused at 850°C for 3 hours. Ten g of NaOH was dissolved in 200 ml of distilled water and 14.3 g of fused kaolin was added to the NaOH solution. The mixture was stirred until it becomes homogeneous. The mixture was placed in a sealed polypropylene bottle and stored in an oil bath at 60 °C in a programmable electrical furnace for 48 hours. The product obtained was filtered and washed with distilled water for several times until pH value dropped to 8.5 after that the product was dried in an electrical oven for 48 hours at 100 °C followed by calcination at 550 °C for 2 hours.

Characterization and Analysis of Prepared NaX Zeolite

The prepared catalyst was characterized by using different technical analysis techniques such as: X–Ray Diffraction (XRD), Atomic Force Microscope (AFM), BET specific surface area and pore volume by ISO-9277-2010 method, sodium content by ASTM D-1428-64 method, and X-ray Fluorescence (XRF) to determine the silica content and silica to alumina ratio.

Results and Discussion

The XRD pattern of prepared zeolite is shown in Figure 1. The patterns indicated that the prepared samples have the structure of zeolite NaX when it's compared with stander structure that shown in Figure 2.

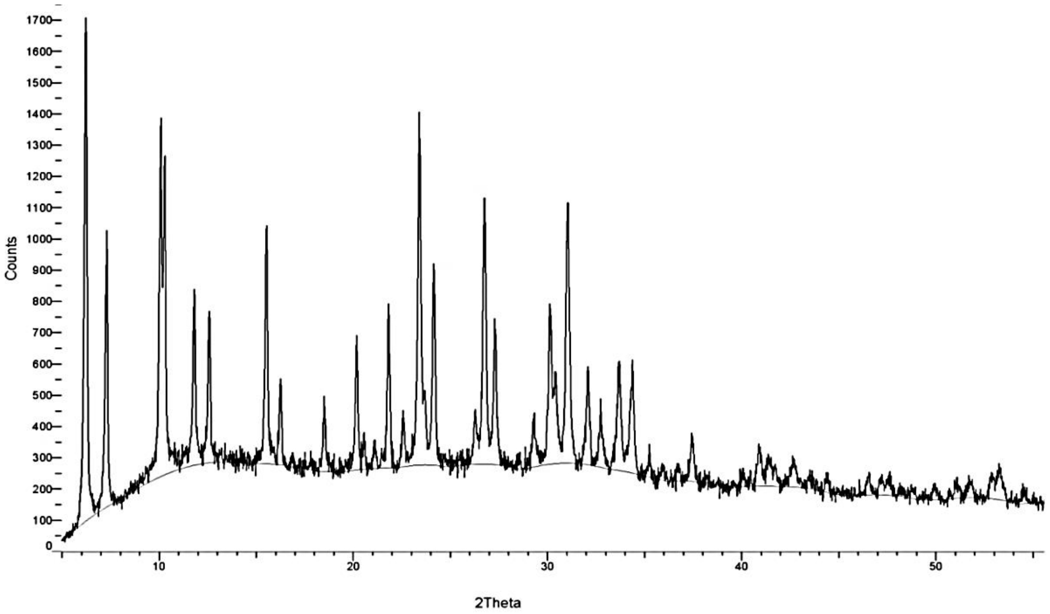

Fig. 1: XRD pattern of prepared zeolite-X

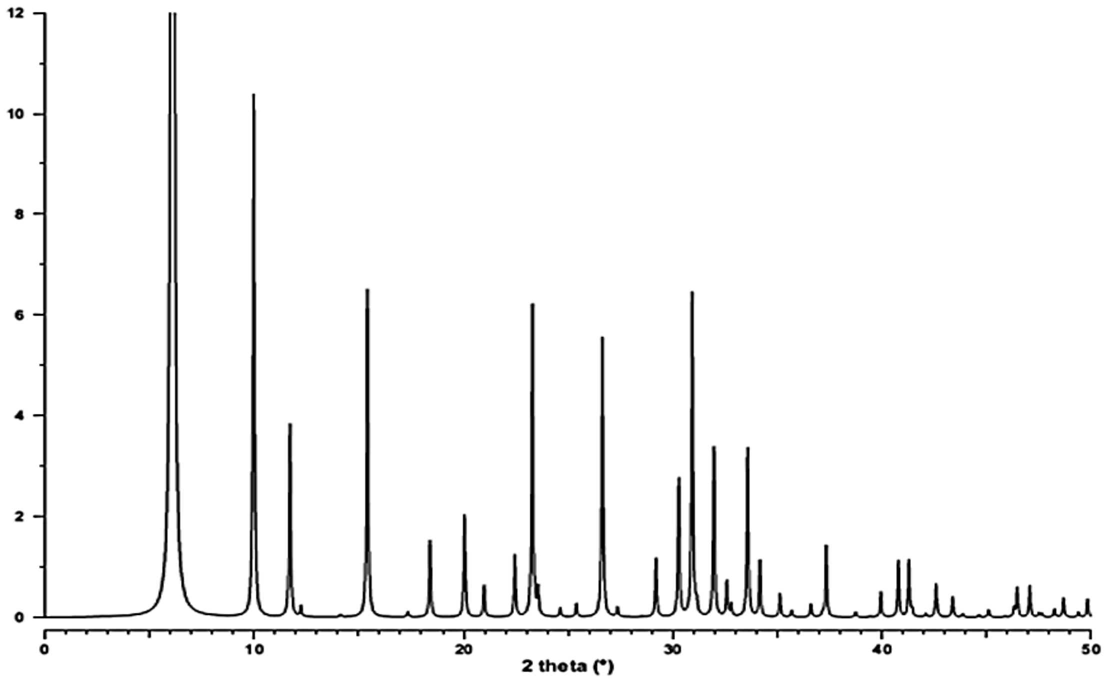

Fig. 2: XRD pattern of standard zeolite-X [29]

The comparison between diffraction angle and lattice spacing of prepared and standard NaX zeolite is shown in Table 2.

Table 2: Angle of diffraction and lattice space for prepared and standard of NaX zeolite

Prepared catalyst		**Standard of catalyst**	
Angle (2Theta) deg.	**d, spacing (Å)**	**Angle (2Theta) deg.**	**d, spacing (Å)**
6.21	14.20	6.12	14.45
10.11	8.73	10.00	8.84
11.80	7.49	11.73	7.54
12.57	7.03	12.25	7.22
15.51	5.70	15.43	5.74
18.49	4.79	18.42	4.81
20.15	4.40	20.07	4.42
21.10	4.20	21.00	4.23
22.56	3.93	22.47	3.95

The silica to aluminum ratio (Si/Al) of NaX zeolite was equal to 1.17 according to XRF analysis which lie in the range of Si/Al ratio of X zeolite [30] also these results were in a good agreement with the result published by Franus [31] who mentioned that the ratio of silica to alumina in NaX is about 1.2. Where the BET surface area and pore volume of NaX zeolite was 255m^2/g and 0.198 cm^3/g respectively with sodium content equal to 9.6 wt.%.

The particle size distribution of prepared NaX from the AFM analysis is shown in Figure 3, while the average nano particle of NaX zeolite was equal to 77.63 nm this result is in a good agreement with the result by Ghasemi and Younes [32] they recorded the Na–X nanocrystals with crystallite size ranging from 70 to 260 nm.

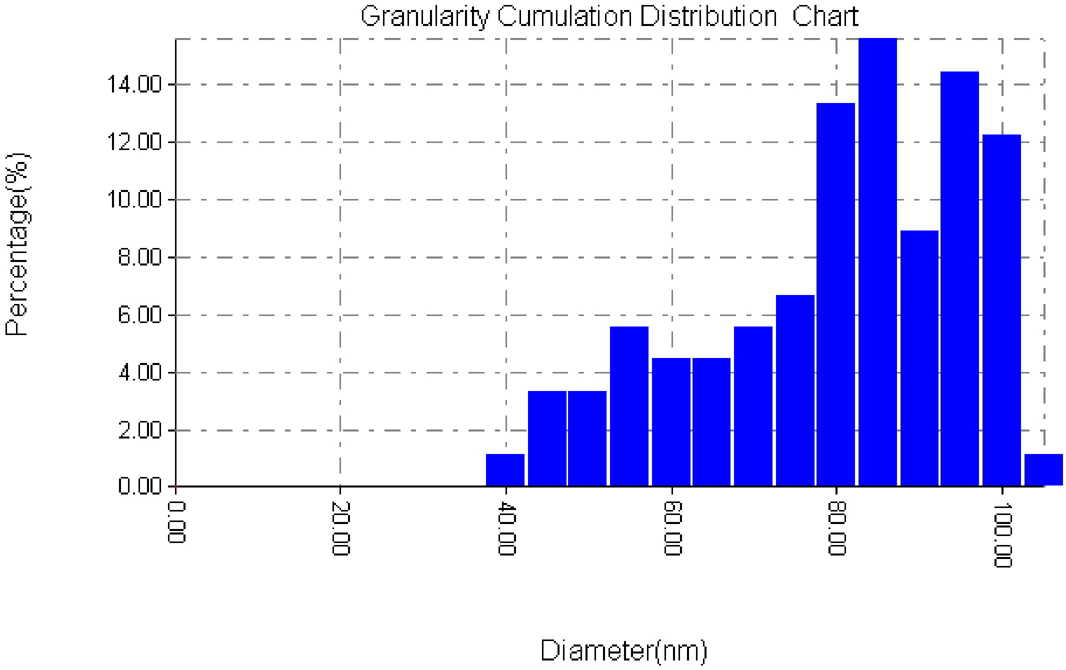

Fig. 3: Bar chart of particle size distribution for prepared NaX zeolite

Thermal Degradation

The thermal decomposition behavior was study by TGA analyzer apparatus. Two samples prepared to analyze first one by using 20 mg of the HDPE and the second one (18 mg of NaX zeolite mixed with 2 mg of HDPE).The two samples were placed separately on the sample holder and pyrolyzed in nitrogen atmosphere in each experiment. Thermogravimetric analyses of composites were done with the temperature range from 25 to 550 °C and the TGA and DTGA data were recorded at different heating rate (4, 7 and 10 °C/min). The TGA figures of thermal pyrolysis (sample HDPE) and catalytic pyrolysis in presence of NaX zeolite (sample HDPE+NaX) are shown in Figures 4 and 5 respectively at different heating rates.

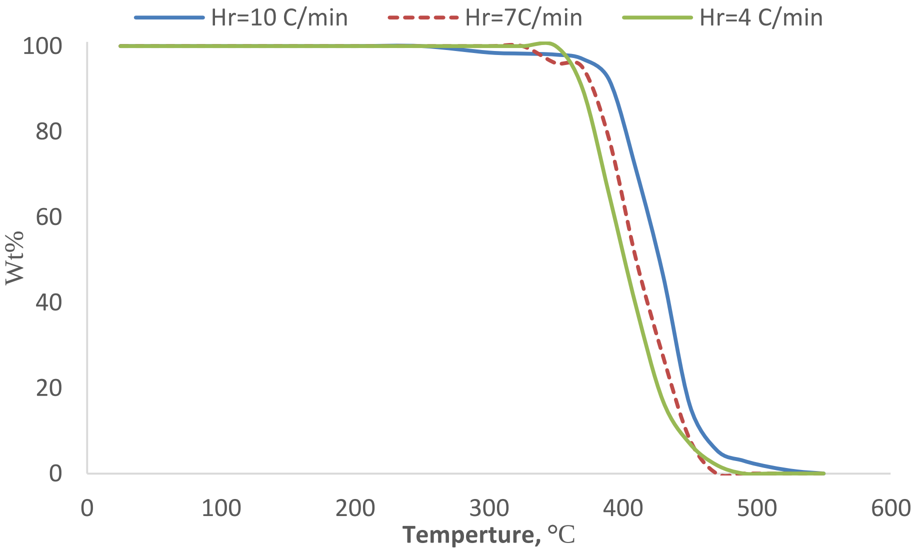

Fig. 4: TGA analysis of HDPE

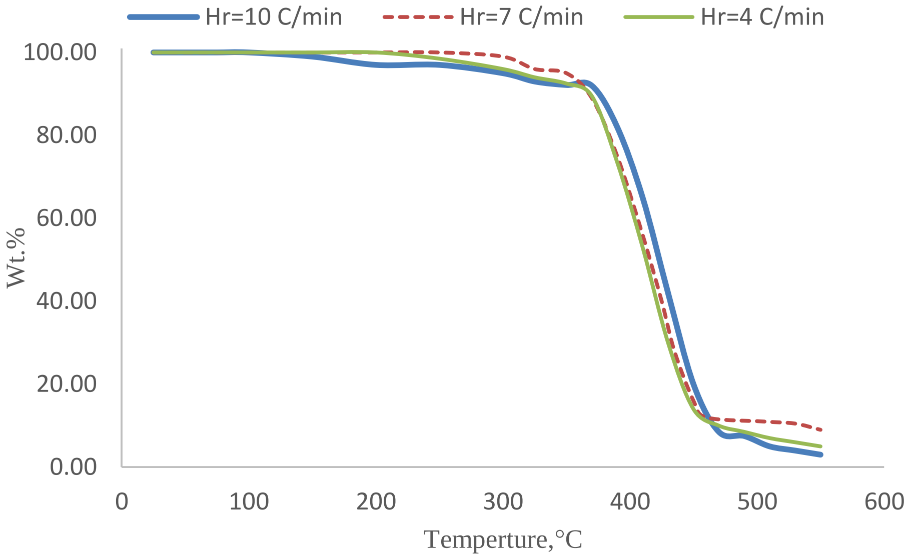

Fig. 5: TGA analysis of HDPE+NaX

In Figures 4 and 5 the weight loss began slowly then rise gradually followed by the main weight loss zone for all samples that because the HDPE mass starts to change after the first bonds are broken, and when the cracking products are light enough to vaporize to the gas phase. It can be observed that the weight change is very rapid [7] [2].

It is clearly in Figures 4 and 5 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 sample reaches degradation temperature in a shorter time when higher heating rates are considered [7] [33] this behavior also realized by Kumar and Singh [27].

In the TGA curve the initial temperature at which the degradation started (T_i) and final temperature at which the degradation completed (T_f) for each sample is shown in Table 3.

Table 3: Started and final temperature of thermal and catalytic HDPE degradation

Heating rate, °C/min	**Pyrolysis temperature range (T_i - T_f), °C**	
	HDPE	**HDPE+NaX**
4	370.2-492.8	265-550
7	370.9-463.9	300-550
10	381-526	282-550

Table 2 was shown when the heating rates increased, the initial and final degradation temperature for HDPE tend to increased too that because polymer molecules does not have enough time to exhaust the heat with increasing heating rate, leading to slower degradation rate and higher degradation temperature due to slow diffusion of heat in both thermal and catalytic degradation [27]. ABOULKAS et.al [34] denoted that the degradation of HDPE start at 381 and complete at approximately 581 °C for different heating rate. The pyrolysis reaction in presence of NaX zeolite start at lower temperature than that of thermal pyrolysis as shown in Table 2 which explain the activity of catalyst.

Coats and Rededfern (CR) Kinetic Method

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

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

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

$$X = \frac{Wi-W}{Wi-Wf} \qquad \ldots(2)$$

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:

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

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

$$f(x) = (1-X)^n \qquad \ldots(4)$$

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

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

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

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

Equation 6 represents the differential form of the non-isothermal rate law. The integral method based on Coats and Redfern (CR) equation is used in this paper, and the approximate integration of Eq. 6 gives:

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

if n=1 $\qquad\qquad\qquad\qquad\qquad\qquad$ ...(7)

$$\ln\left[\frac{-\ln(1-X)^{1-n}}{(1-n)T^2}\right] = \ln\frac{AR}{H_rE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{RT} \text{ if } n\neq \mathbf{1} \qquad \ldots(8)$$

The above two equations are the Coats-Redfern method. The plot of $\ln[-\ln(1-X)/T^2]$ versus 1/T becomes a linear line for n=1; the plot of $\ln[1-(1-X)^{1-n}/T^2$versus 1/T is also a linear line for n≠1. 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 [35] [36] [1].

The Coats Redfern method was used to estimate the activation energy at each heating rate by applied Equation 7 at 4, 7 and 10 °C/min heating rate for two samples: HDPE alone and HDPE+NaX. The plots of CR method for two samples are shown in Figures 6 and 7.

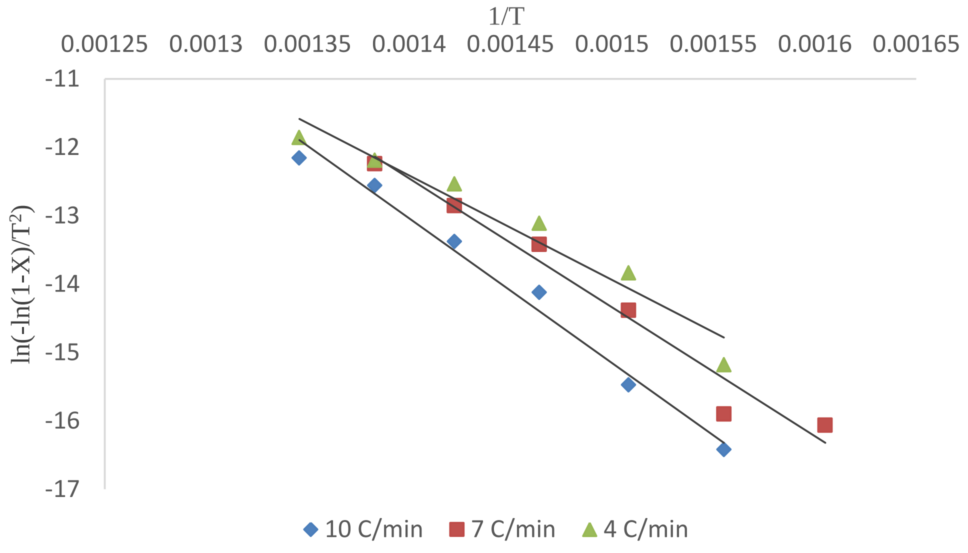

Fig. 6: CR plots at different values of conversion for pyrolysis of HDPE

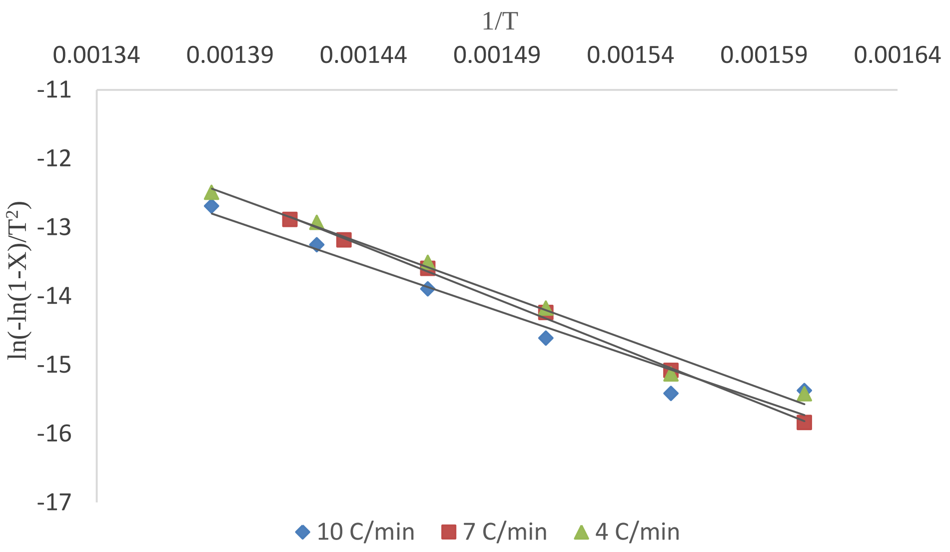

Fig. 7: CR plots at different values of conversion for pyrolysis of HDPE+NaX

Figures 6 and 7 were show the typical plot of ln [–ln (1 – x)/T^2] vs. 1/T for 4, 7 and 10 °C/min for two samples. Reasonable fits of data to straight lines in this figure indicate that the assumption of first-order kinetics for thermal and catalytic pyrolysis of HDPE is acceptable [7] [27]. The values of Ea and A from CR method are shown in Table 4.

Table 4: Activation energy and pre-exponential factor by CR method

Hr [°C/min]	**HDPE**		**HDPE+NaX**	
	Ea [kJ/mol]	**lnA [min^{-1}]**	**Ea [kJ/mol]**	**lnA [min^{-1}]**
4	127.00	20.00	117.38	18.03
7	156.62	25.71	128.21	20.53
10	175.87	28.84	109.68	17.24

Table 4 shows the kinetic parameters that were determined at different heating rates. For all samples Ea and A are dependent on heating rate and tends to increase as heating rate increases. The average activation energy values by CR method for thermal and catalytic pyrolysis of HDPE are 153.16 and 118.42 kJ/mol respectively.

Activation energy increased with increase in heating rate as a result of very low thermal conductivity of polymeric material and therefore the temperature distribution in the HDPE will be significant at a high heating rate [27].

The different in values of both activation energies and frequency factors at a different heating rate are attributed to variations in thermal lag at different heating rates [1].

The values of Ea in Table 4 indicated that the presence of nano-catalyst NaX decrease the activation energy of HDPE pyrolysis compared with thermal pyrolysis. Park et al. [37] reported that the Ea for HDPE alone equal to 123 kJ/mol at10 k/min by CR method.

Conclusion

Nano NaX zeolite with 77.63 average nano particles was prepared by used kaolin as source of silica and alumina under hydrothermal condition. The silica to alumina ration for prepared NaX zeolite was 1.17. The activity of NaX zeolite was tested in the pyrolysis of HDPE.

The kinetic parameters of HDPE decomposition under non-isothermal conditions using TGA were determined. The TGA analysis was shown that the main thermal and catalytic pyrolysis process occurred in the temperature range 282 to 550 °C. The average activation energy values of thermal and catalytic pyrolysis of HDPE have been calculated by CR method was 153.16 and 118.42 kJ/mol respectively for first order decomposition reaction at different heating rates.

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