IAU-ARAK

J. Iran. Chem. Res. 2 (2009) 195-210

Journal of the
Iranian
Chemical
Research

www.iau-jicr.com

Thermal and catalytic degradation study of polyethylene and investigation the catalytic effect of X-Zeolite and Silica-Alumina on degradation kinetic

Mohammad Taghi Taghizadeh *, Parinaz Seifi-Aghjekohal, Ali Bahadori, Banafsheh Zeraatkar

Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Received 24 May 2009; received in revised form 28 July 2009; accepted 10 August 2009

Abstract

The thermal degradation of polyethylene (PE) was carried out in the absence and presence of catalystes X-Zeolite and Silica-Alumina at different temperatures. The optimum PE/Catalysis ratio was 0.25:0.05 g/g, which produced highest degradation value. PE and PE/Catalysis were characterized by thermogravimetric analysis. The thermal degradation properties of polymer have been studied by Infrared spectroscopy–FT-IR. Experimental data indicated that the presence of catalysis greatly increased the rate of degradation of PE. The activation energy of degradation for pure polyethylene and polyethylene in presence catalysises was calculated by Arrhenius equation and Ozawa method. Activation energy follows the order PE < PE/Silica-Alumina < PE/X-Zeolite.

Keywords: Thermal degradation; Polyethylene; X-Zeolite; Silica-Alumina; Activation energies.

1. Introduction

As a conventional plastic material, polyethylene (PE) is widely used in food packaging or food service, retail industry and agriculture field. It is almost inevitable that PE will continue to play an essential part in the commodities in spite of its resistance to microbial or enzymatic degradation [1]. Polyethylene is a major component of plastic waste from domestic refuse. Due to their chemical stability and unbiodegradability, waste PE products are being mainly disposed by the incineration, which will release a lot of toxic by-products. Its efficient reutilization has a growing importance these years due to the increased demand for resource recycling and environmental protection. Fundamental research on pyrolysis of plastic waste including polyethylene is therefore a topical subject.

Many papers on pyrolysis kinetics of polyethylene have appeared in literature [2–5]. Between various polymer recycling methods, thermal and/or catalytic degradation of plastic waste to fuel show the highest potential for a successful future commercial process, especially as plastic waste can be considered as a cheap source of raw materials in times of accelerated depletion of natural resources.

Pure thermal degradation of plastic wastes needs high temperatures and produces heavy products that need further processing for their quality to be upgraded. On the other hand, the presence of catalysts, such as zeolites, reduces the process temperature and forms hydrocarbon

---

* Corresponding author. Tel.: +98 411 3393137; fax: +98 411 3340191.
E-mail address: mttaghizadeh@ tabrizu.ac.ir (M.T. Taghizadeh)

products in the motor fuel boiling range, which eliminates the need for further upgrading process steps.

Catalytic degradation occurs at considerably lower temperatures and forms hydrocarbons in the range of motor engine fuel, eliminating the necessity of further processing [6–10]**.** Catalytic degradation is usually carried out on acid sites with sufficient strength, and thus various solid acids have been tested as catalysts [11]. For such a catalytic process mainly zeolite-based catalysts [6, 7, 10, 12] have been used, as well as silica–alumina [13, 14], clay-based catalysts [8–10] and MCM-type mesoporousmaterials [15].

The effect of catalysts on polymer degradation has also been examined, particularly the degradation of polyethylene (PE) and polypropylene (PP) over silica-aluminaand zeolite catalysts [16, 17]. Karishma Gobin, George Manosstudied studied the catalytic cracking of linear low density polyethylene (lldPE) by thermogravimetric analysis (TGA). They used the various catalysts such as US-Y zeolite, ZSM-5 zeolite [18]. G.J.T. Fernandes and et. al studied the degradation of high-density polyethylene (HDPE) was studied alone and in presence of silicoaluminophosphate as a catalyst. They observed that the activation energy decreased from 290 kJ mol−1 for HDPE alone; to 220 kJ mol−1 for 25%SAPO-37/HDPE, evidencing that SAPO-37 is an effective catalyst for polyethylene degradation [19].

Liliana and et. al studied the thermal-catalytic transformation of High-density polyethylene (HDPE) over Zn-ZSM-11, ZSM-11 and Zn-MCM-41 zeolites as catalysts.They showed that the catalytic transformation of the polyolefin occurs at lower temperature with respect to thermodecomposition of the pure HDPE [20]. Ji Won Park,and et. al studied the effect of pore shape on catalytic activities of zeolites and they showed that the pore shape of the zeolites was important in determining activity and product selectivity in the degradation of polymers by influencing the diffusion rate of cracked products and suppressing the formation of large molecules [21].

The results obtained from Isabel C. Neves and et.all show that the efficiency of different zeolites was due to their acidity. A high Si/Al ratio gave a greater acidity to zeolites and the onset degradation temperature of the polymer and related activation energy decreased [22]. Manos’s research group has performed several studies concerning,the catalytic degradation of PE over different zeolite,structures. It was shown that zeolites possessing strong acid sites accelerated the PE degradation [23]. Therefore, in this study, we are going to focus on investigate the role of catalysis on degradation behavior of PE at different concentration of catalysis and to find beast concentration of catalysis for increase rate of degradation of polymer. The kinetics model was used to determine the degradation rate. The activation energies were calculated from Arrhenius equation and Ozawa method. The thermal degradation behavior of polymer has been studied by (TG) and (FT-IR).

2. Experimental

2.1. Materials

Polyethylene (M_v =87000), was purchased from (IRAN) was used without purification. The X-Zeolite was obtained from Merck with the specific surface area of 178 $m^2\ g^{-1}$, were used in powder form whose primary particles ranged in 2.2–7.4 A^o diameters. Silica-Alumina was obtained from Merck whose primary particles ranged in 4 A^o diameters were used in powder form. Methanol (MW=32.04) and Dekaline (MW=138.25) from Merck and Xylene (MW=106.17) from Fluka was used.

2.2. Preparation of the samples

Pure polyethylene (PE) is used without purification. To investigate the role of catalyst on degradation behavior of PE, samples were prepared by mixing 0.25 g of polymer powder with different mass percents of X-Zealot and SA at room temperature. The final product were placed onto a dish for investigate degradation behavior.

2.3. Analytical Techniques

2.3.1. Thermal degradation

The dynamic and isothermal degradation studies were carried out by using 0.25 g of the purified PE and polymer/catalyst (gas flow of 0.050 dm^{-3} min^{-1}) in a TGA DTG-60AH thermal analyzer. For the dynamic experiments, the samples were heated from 270 to 500 °C at a heating rate varying from 1.5 °C min^{-1} to 2.5 °C min^{-1} while the loss of mass was monitored.

For the isothermal experiments the samples were heated at a rate of 10 °C min^{-1} to 150 °C, maintained at this temperature for 10 min and then heated at a rate of 20 °C min^{-1} to the desired temperature. The zero time for the thermal degradation study was taken in the moment at which the temperature stabilized.

2.3.2. Infrared spectroscopy–FT-IR

The Fourier Transform IR spectra (FT-IR) of unheated and thermally degraded samples were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer, between 500 and 4000 cm^{-1}. The samples were analyzed as KBr pellets.

3. The kinetic parameters

The kinetic parameters of a thermal decomposition reaction can be evaluated by dynamic and isothermal experiments. In the former case, the sample is heated from the room temperature until its complete decomposition at a linearly programmed rate while in the latter case several isothermal experiments are carried out for different periods of time at a temperature close to the degradation temperature.

The kinetic expression describing the dependence of the extent of conversion for thermal decomposition of a polymer on the reaction time, in an isothermal experiment, is given by:

$$r = \frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (1)$$

where n is the reaction order ,k is the rate constant and α being the extent of conversion, given by:

$$\alpha = \frac{W_e}{W_o} \qquad (2)$$

where W_e is the mass of polymer evolved as volatile fragments and W_0 is the initial mass.
The integration of Eq. (1) results in:

$$-\ln(1-\alpha) = kt + c \qquad (3)$$

by plotting $-\ln(1-\alpha)$ versus of the time of the degradation will yield the straight line whose slope is k.

The k with activation energy follows an Arrhenius relationship (Eq. (2)) for the beginning of the reaction.

$$k = A\exp(\frac{-E_a}{RT}) \qquad (4)$$

Plot of *LnK* versus *1/T* yields a straight line which the activation energies, E_a, obtained from the slopes of the lines. If, instead of an isothermal experiment, a dynamic experiment is performed, the temperature, *T*, changes linearly from the initial temperature, T_0, according to the heating rate, *a*, during the time *t*, then:

$$T = T_o + at \qquad (5)$$

The kinetic of thermal decomposition of a polymer is given by [24]:

$$r = -\frac{dw}{dt} = kw^n \qquad (6)$$

The amount of kw^n can be represented by the following equation:

$$kw^n = A\exp(-E_a / RT)w^n \qquad (7)$$

where *w* is residual weight of samples and *t* is time.

According to Doyle's approximation [25] and Eq. (6) can be expressed as:

$$\int_{wo}^{w} -\frac{dw}{w^n} = \frac{A}{a}\int_{To}^{T} \exp(-\frac{E_a}{RT})dT = \frac{A}{a}\frac{E_a}{R}P(\frac{E_a}{RT}) \qquad (8)$$

The amount of *P* can be represented by the following equation:

$$\log P(\frac{E_a}{RT}) = \lambda + \mu(E_a / RT) \qquad (9)$$

where λ *and* μ are Doyle's constant.

The integration of Eq. (7) and its substitution in Eq. (9) results in:

$$\log F(w) = \log A + \log E_a - \log R - \log a + \lambda + \mu\frac{E_a}{Rt} \qquad (10)$$

$$\log a = v + (\mu\frac{E_a}{R})\frac{1}{T} \qquad (11)$$

where $v = \log A - \log F(w) + \log E_a - \log R + \lambda$ and μ=-0.4567.

The activation energy is determined from the slope of the straight line which results by plotting logarithm of heating rate versus 1/T.

4. Results and Discussion

4.1. FTIR analysis of PE

The functional groups in PE were characterized by FT-IR spectroscopy. Fig. 1 compares FT-IR spectra of PE samples before and after degradation at 370 and 390 °C temperature for 30 min. The most characteristic bands in the infrared spectrum of PE are (a) the strong band centered at 1467 Cm^{-1} which is attributed to methylene group and the bending vibrations of C-H bonds out of plan; (b) the band corresponding to the asymmetric and axial stretching of methylene which is centered at 2916 Cm^{-1}; (c) the band corresponding to the symmetric stretching of methylene which is centered at 2848 Cm^{-1}; (d) the band centered at 719 Cm^{-1}, corresponding to bending vibrations and deformation of C-H bonds in of plan; (e) the band at 1635 Cm^{-1} resulting C=O band.

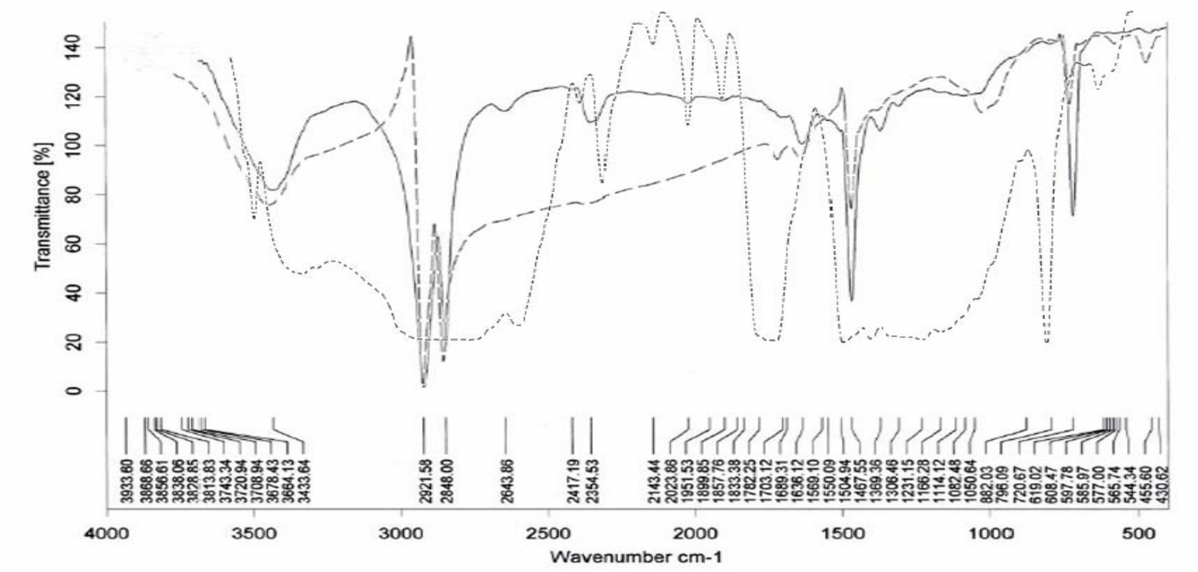


Fig. 1. Infrared spectrum of PE before and after degradation. —— before degradation, - - - after degradation at 370 °C, 390 °C for 30 min.

Fig. 1 also shows the degraded PE samples after 30 min of degradation at 370 ^{o}C and lower intensity of characteristic alkyl peaks compared with the original PE sample. As can be seen from Fig. 1, the structure of polymer is entirely changed at 390 ^{o}C. For the degraded PE sample at 390 ^{o}C, a new peak at 1700-1760 cm^{-1} appears which can be attributed to carbonyl groups. The proportion of this peak increased with increasing of temperature [26].

4.2. Isothermal studies on the thermal degradation of PE of PE

In the isothermal experiments, PE was heated at four temperatures, 360, 370, 380 and 390 ºC and it was maintained at these temperatures for a given time while the loss of weight was monitored. Extension of conversion as a function of the reaction time calculated by treating the data issued from the isothermal experiments and Eq. (2). The results are shown in Table 1.

By plotting $-\ln(1-\alpha)$ versus of the time of the degradation will yield the straight line whose slope is k (Table. 2). Then, the curves Lnk versus $1/T$ were plotted for experimental data in this range of α, allowing the determination of the kinetic parameter E_a from the slope of the resulting straight line as $Ea = 131.1$ kJ mol^{-1}, (Eq. 4).

As can be seen from data of Table 2, the rate constant of degradation increases with increasing temperature. This is only consequence of the fact that rate of degradation of PE increases with increasing temperature.

4.3. Dynamic studies on the thermal degradation of PE

In the dynamic experiments, PE was degraded with three heating rate (1.5, 2.0 and 2.5 K min^{-1}). The TG curves of PE recorded from 270 to 500 ºC and are shown in Fig. 2. The activation energy for the thermal degradation of PE was determined from the TG curves using the method described in section (3). According to Eq. (11) it has been found that slope of curve logarithm of heating rate versus reciprocal temperature to reach a conversion level has relation with activation energy. Therefore, the temperature to reach a specific polymer mass fraction from 10% to 90% was determined; these data for every heating rate are reported in Table 3.

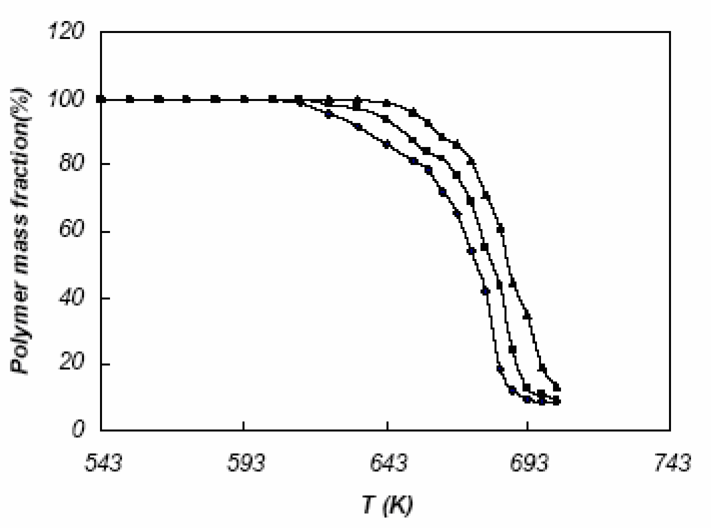
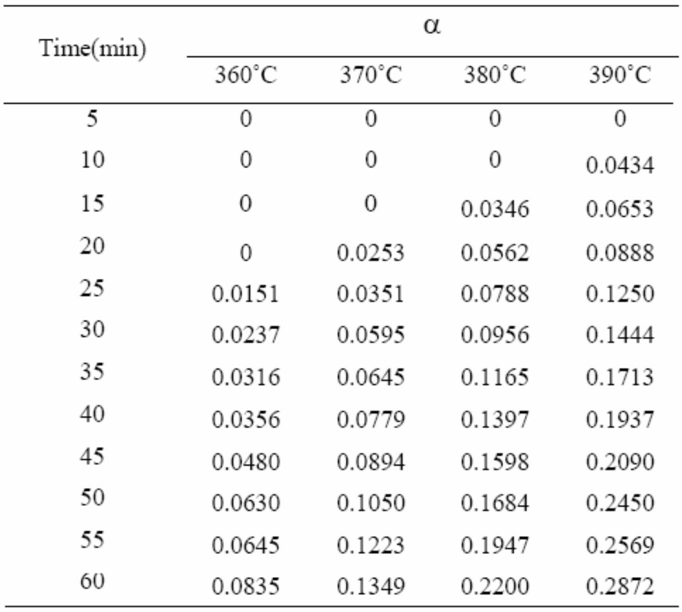


Fig. 2. TG curves of PE at various heating rate. Heating rate —♦—1.5 K/min, —■—2 K/min K, —▲— 2.5 K/min.

Table 1
Extension of conversion as a function time for PE at different temperatures.

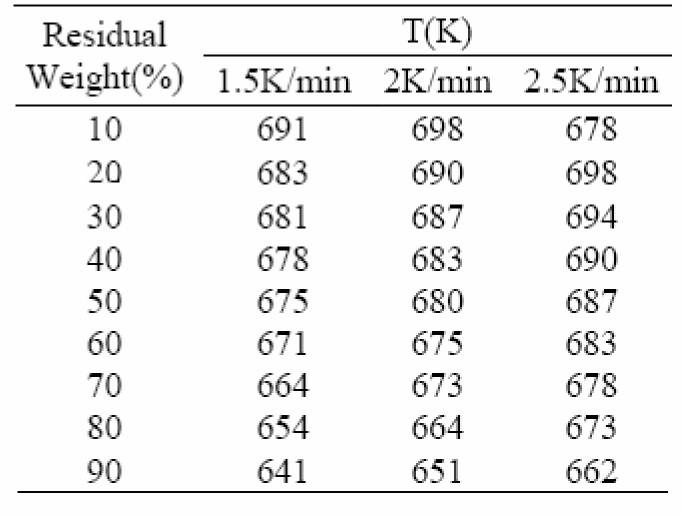


Time(min)	α			
	360˚C	370˚C	380˚C	390˚C
5	0	0	0	0
10	0	0	0	0.0434
15	0	0	0.0346	0.0653
20	0	0.0253	0.0562	0.0888
25	0.0151	0.0351	0.0788	0.1250
30	0.0237	0.0595	0.0956	0.1444
35	0.0316	0.0645	0.1165	0.1713
40	0.0356	0.0779	0.1397	0.1937
45	0.0480	0.0894	0.1598	0.2090
50	0.0630	0.1050	0.1684	0.2450
55	0.0645	0.1223	0.1947	0.2569
60	0.0835	0.1349	0.2200	0.2872

Table 2
Rate coefficients data for PE at different temperatures.

T(K)	K(1/min)
633	0.0019
643	0.0027
653	0.004 0
663	0.0049

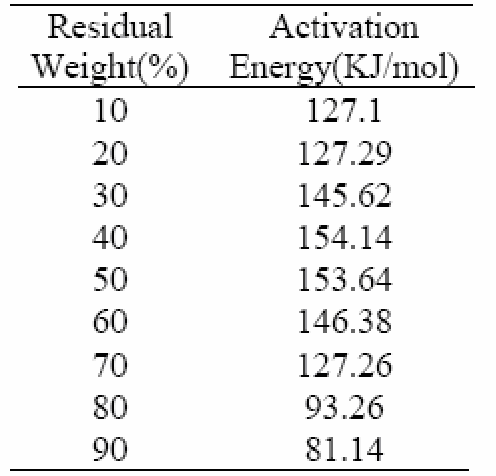
Table 3
To reach a specific polymer mass fraction data from 10% to 90% for PE at different temperatures.



Residual Weight(%)	T(K) 1.5K/min	2K/min	2.5K/min
10	691	698	678
20	683	690	698
30	681	687	694
40	678	683	690
50	675	680	687
60	671	675	683
70	664	673	678
80	654	664	673
90	641	651	662

The activation energies for every polymer mass fraction were determined from the slopes of curve of logarithm of heating rate versus 1/T and they are reported in Table 4. The overall activation energy for the degradation of PE calculated from average activation energies as *E*a = 128.43 kJ mol^{-1}.

Table 4
The activation energies for PE at different mass fraction.



Residual Weight(%)	Activation Energy(KJ/mol)
10	127.1
20	127.29
30	145.62
40	154.14
50	153.64
60	146.38
70	127.26
80	93.26
90	81.14

4.4. Study on the thermal degradation of PE/ catalyst

4.4.1. Preparation of optimum value of catalyst

To investigate the role of catalyst concentration on degradation behavior of PE and to achieve optimum concentration of catalyst, degradation behavior of PE/Catalyst studied at different mass of catalyst, (0.02, 0.03, 0.04, 0.05 and 0.07 g) and was followed by extent of conversion. Data of the degradation of PE/X-Zeolite and PE/Silica-Alumina in different concentrations (0.02 to 0.07 g) at 370 ^{0}C are shown in Figs. 3 and 4, respectively. As indicated by these figures, the extent of degradation gradually increases with increasing concentration of catalyst but after a specific concentration, the extent of degradation decreases. These results demonstrate that concentration of catalyst has a suitable affect on degradation of polymer, but among the investigated samples, sample with 0.05 g of catalyst (16% W) has the highest value thermal degradation.

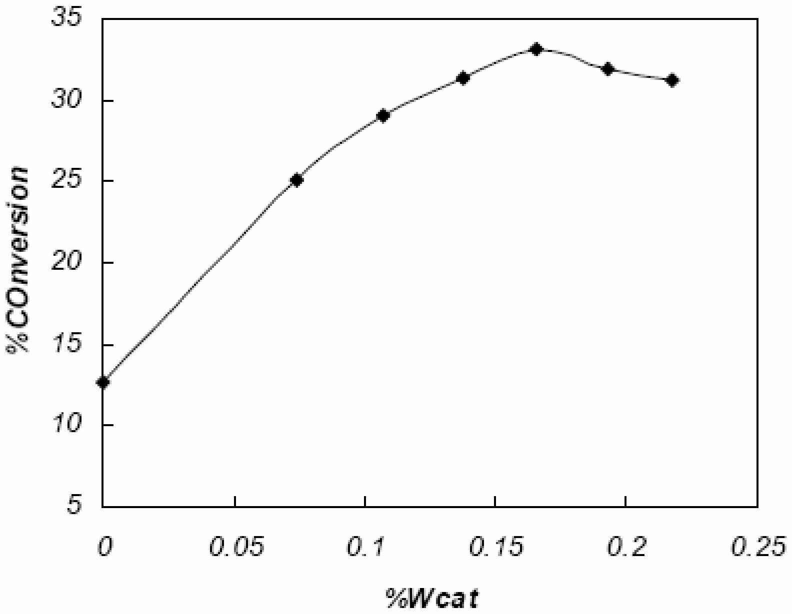


Fig. 3. Curves of optimum concentration of X-Zeolite for degradation of PE at 370 ºC.

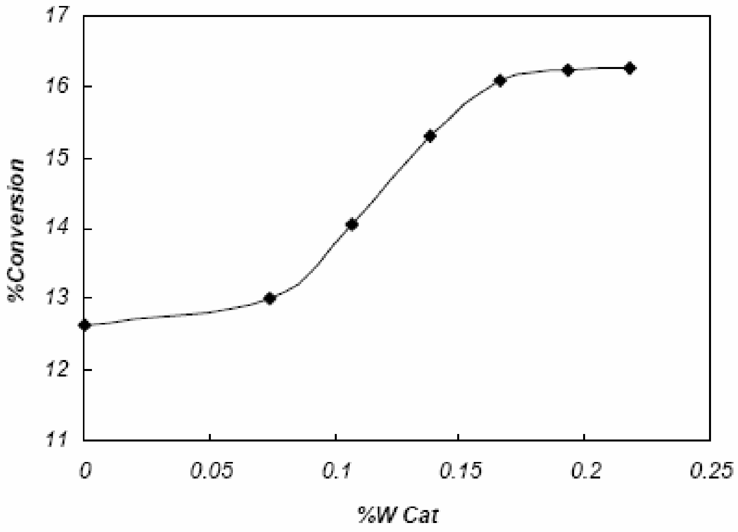


Fig. 4. Curves of optimum concentration of Silica-Alumina for degradation of PE at 370 ºC.

4.4.2. Calculation of activation energy of PE/ catalyst in isothermal condition

To investigate the role of catalyst on activation energy, degradation of PE/Catalyst with 16% W of catalyst studied at four temperatures, 360, 370, 380 and 390 ºC (isothermal degradation). Extension of conversion as a function of the reaction time calculated by treating the data issued from the isothermal experiments and Eq.(2). The results are reported for X-Zeolite and Silica-Alumina in Tables 5 and 6, respectively. In the case of catalyst, the rate of thermal degradation depends on the concentration of catalyst and polymer as following:

$$R = k|PE|^{\alpha}|Cat|^{\beta} \qquad (12)$$

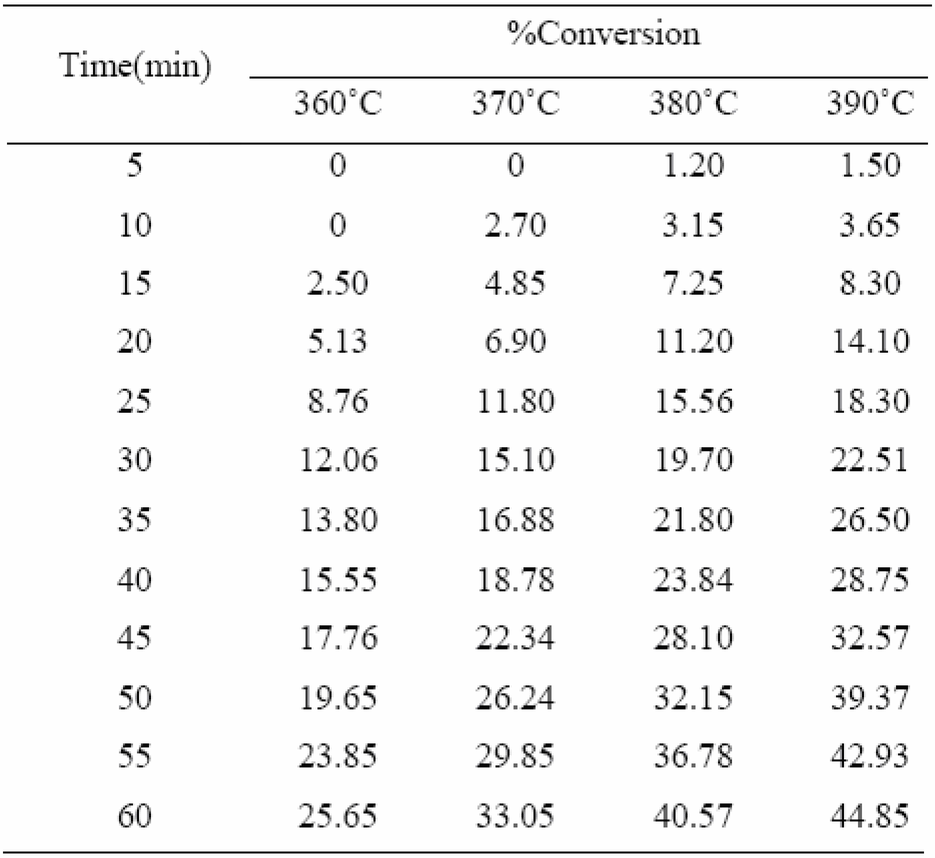
where k is rate constant, defined in Eq.(4), Thus, Eq. (12) may be rewritten as:

$$R = A\exp(-E_a / RT)|PE|^{\alpha}|Cat|^{\beta} \qquad (13)$$

Eq. (13) may be rewritten as:

$$\ln R = (-\frac{E_a}{RT}) + cte \qquad (14)$$

Table 5
Extension of conversion as a function time for PE/ X-Zeolite at different temperatures.



Time(min)	%Conversion			
	360°C	370°C	380°C	390°C
5	0	0	1.20	1.50
10	0	2.70	3.15	3.65
15	2.50	4.85	7.25	8.30
20	5.13	6.90	11.20	14.10
25	8.76	11.80	15.56	18.30
30	12.06	15.10	19.70	22.51
35	13.80	16.88	21.80	26.50
40	15.55	18.78	23.84	28.75
45	17.76	22.34	28.10	32.57
50	19.65	26.24	32.15	39.37
55	23.85	29.85	36.78	42.93
60	25.65	33.05	40.57	44.85

The activation energies for every catalyst were determined from the slopes of curve *lnR* versus *1/T* (Eq.(14)). To achieve the value of R, we used from equation of *Rate=dx/dt*. We know that percent of conversion is relative to variation of concentration; therefore rate of reaction was determined from the slopes of curve of percent of conversion versus time of reaction. These curves are shown in Figs. (5, 6) for X-Zeolite and Silica-Alumina respectively. The activation energies for degradation of PE/X-Zeolite and PE/Silica-Alumina calculated from Eq. (14) are equal with *E*a = 71 kJ mol^{-1} and *E*a = 106.9 kJ mol^{-1} respectively.

4.4.3. Calculation of activation energy of PE/ catalyst in dynamic condition

In the dynamic experiments to investigate the role of catalyst on activation energy, degradation of PE/Catalyst with 16% W of catalyst studied with three heating rate (1.5, 2 and 2.5 K/min). The TG curves of PE/Catalyst recorded from 270 to 500 ºC are shown in Figures 12, 13 for X-Zeolite and Silica-Alumina, respectively

The activation energy for the thermal degradation of PE/Catalyst was determined from the TG curves using the method described in section (3). According to Eq.(11) it has been found that slope of curve of logarithm of heating rate versus reciprocal temperature to reach a conversion level has relation with activation energy. Therefore, by using Figs. 7, 8, the temperature to reach a specific polymer mass fraction from 10% to 90% was determined; these data for every heating rate are reported in Tables 7, 8.

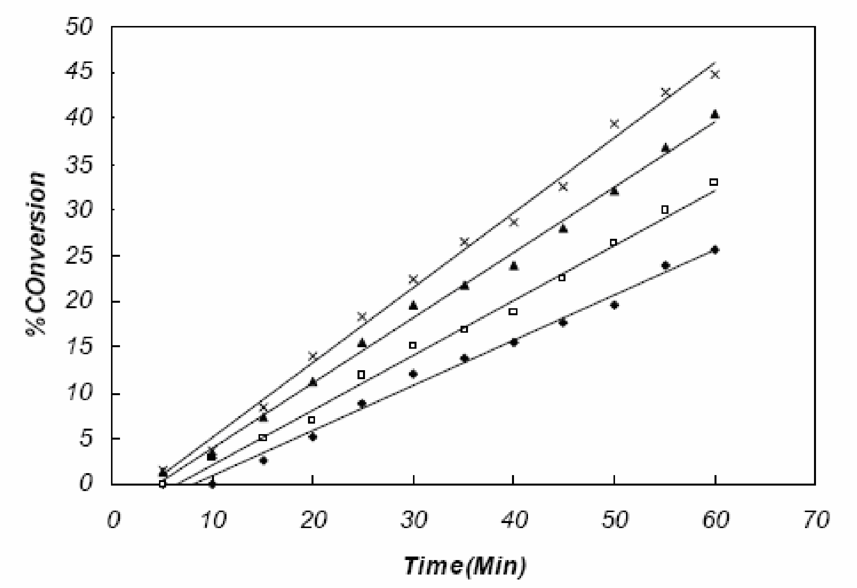


Fig. 5. Curves of percent of conversion versus time of reaction for the isothermal degradation for the thermal degradation PE/X-Zeolite. Time at –●–360 ºC, –□–370 ºC, –▲–380 ºC and –n– 390 ºC.

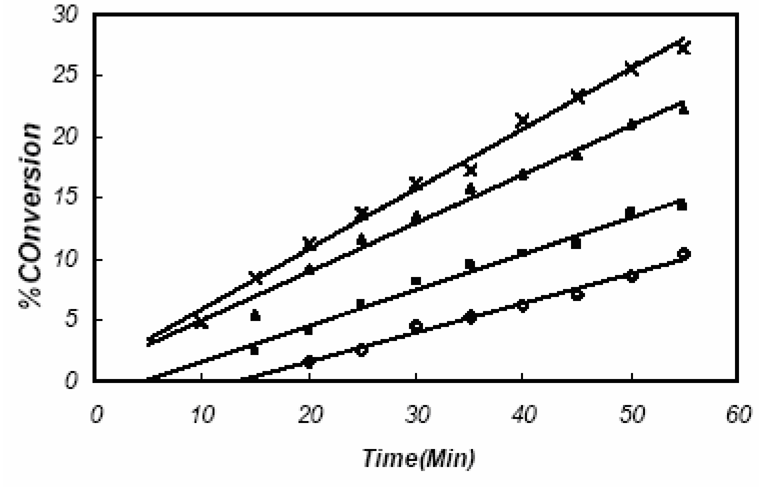
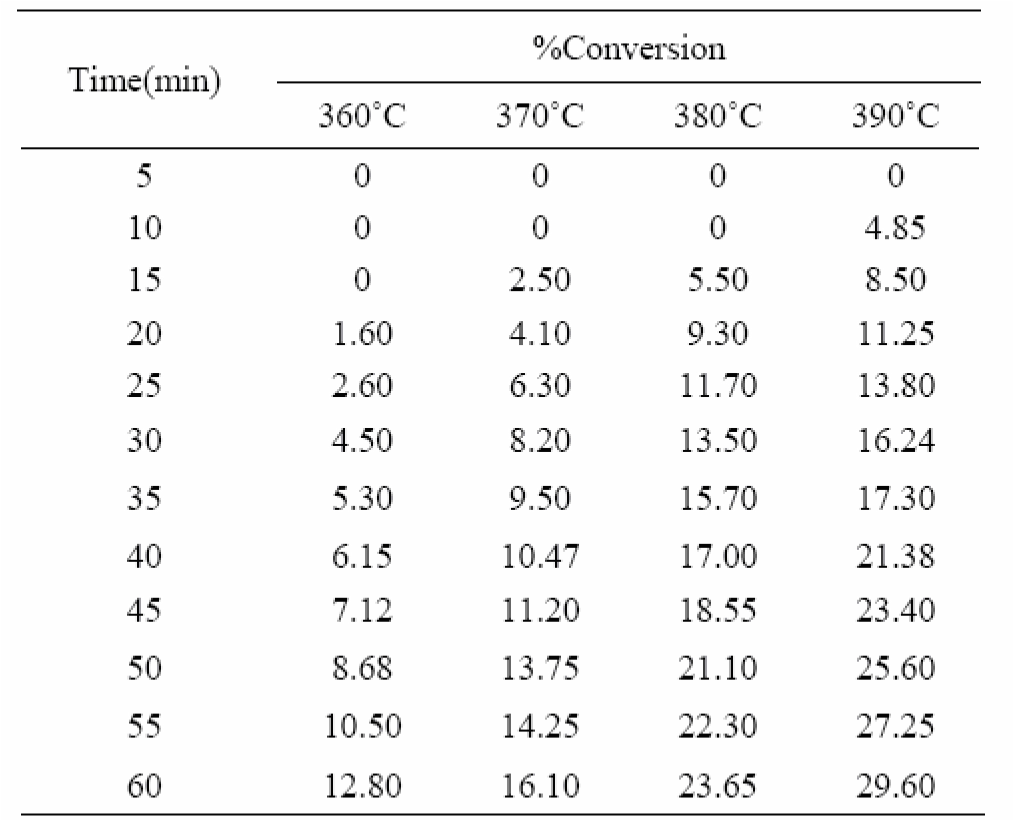


Fig. 6. Curves of percent of conversion versus time of reaction for the isothermal degradation for the thermal degradation PE/Silica-Alumina. Time at –●–360 ºC, –□–370 ºC, –▲–380 ºC and –n– 390 ºC.

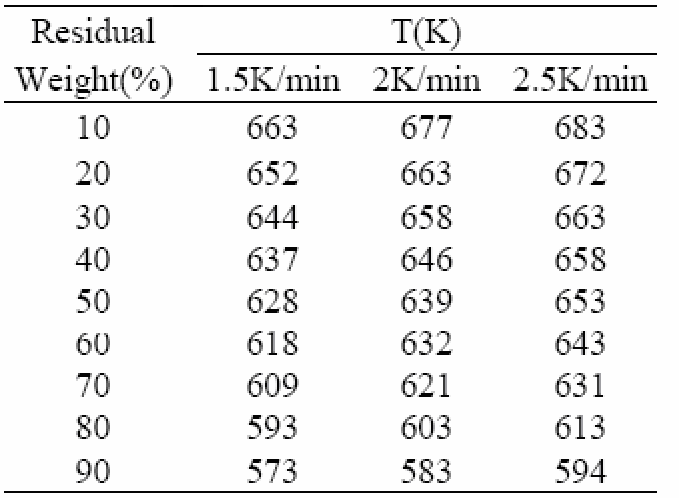
Table 6
Extension of conversion as a function time for PE/ Silica-Alumina at different temperatures.



Time(min)	%Conversion			
	360°C	370°C	380°C	390°C
5	0	0	0	0
10	0	0	0	4.85
15	0	2.50	5.50	8.50
20	1.60	4.10	9.30	11.25
25	2.60	6.30	11.70	13.80
30	4.50	8.20	13.50	16.24
35	5.30	9.50	15.70	17.30
40	6.15	10.47	17.00	21.38
45	7.12	11.20	18.55	23.40
50	8.68	13.75	21.10	25.60
55	10.50	14.25	22.30	27.25
60	12.80	16.10	23.65	29.60

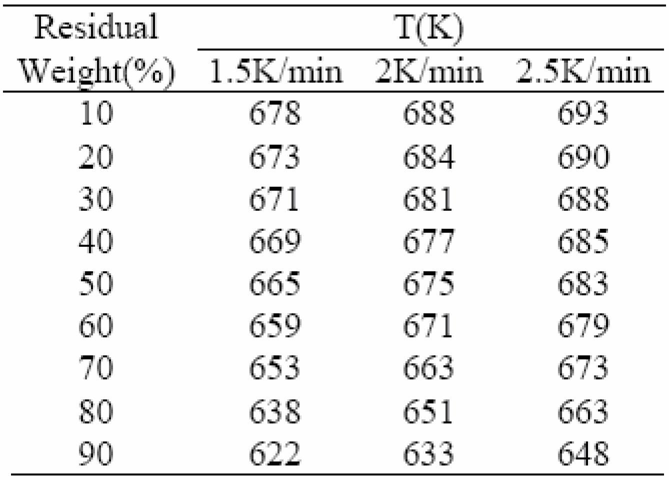
The activation energies for every polymer mass fraction were determined from the slopes of curve logarithm of heating rate versus 1/T (Figures 14,15) and they are reported in Table 9, 10. The overall activation energy for degradation of PE/Catalyst calculated from average activation energies as Ea = 77.8 kJ/mol and Ea = 98.1 kJ/mol for X-Zeolite and Silica-Alumina, respectively.

Table 7
To reach a specific polymer mass fraction data from 10% to 90% for PE/ X-Zeolite at different temperatures.



Residual Weight(%)	T(K)		
	1.5K/min	2K/min	2.5K/min
10	663	677	683
20	652	663	672
30	644	658	663
40	637	646	658
50	628	639	653
60	618	632	643
70	609	621	631
80	593	603	613
90	573	583	594

Table 8
To reach a specific polymer mass fraction data from 10% to 90% for PE/ Silica-Alumina at different temperatures.



Residual	T(K)		
Weight(%)	1.5K/min	2K/min	2.5K/min
10	678	688	693
20	673	684	690
30	671	681	688
40	669	677	685
50	665	675	683
60	659	671	679
70	653	663	673
80	638	651	663
90	622	633	648

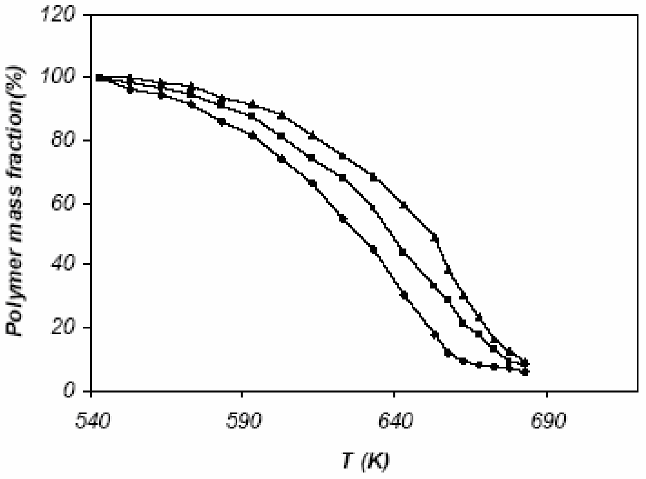


Fig. 7. TG curves of PE/X-Zeolite at various heating rate. Heating rate –♦–1.5 K/min, –■–2 K/min K, –▲–2.5 K/min.

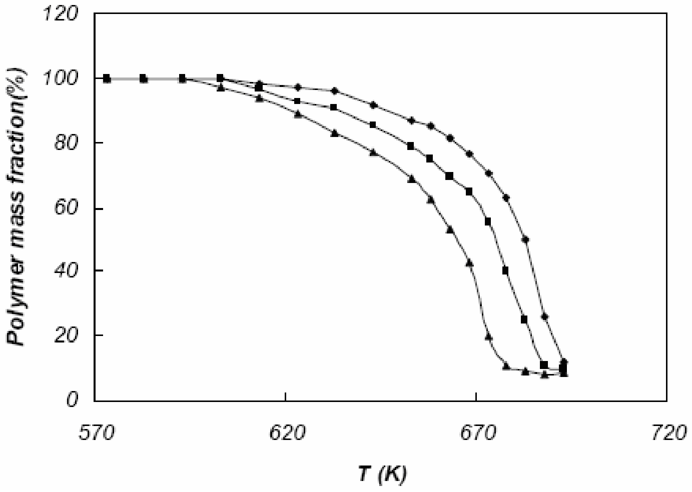
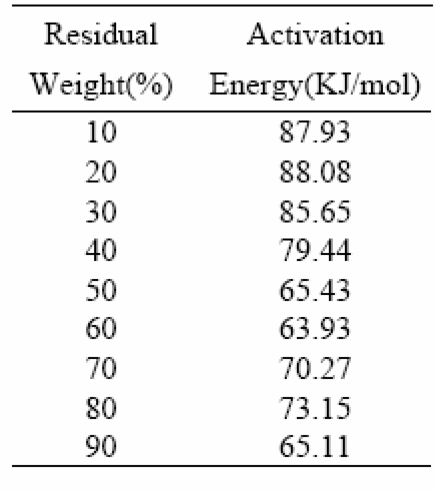


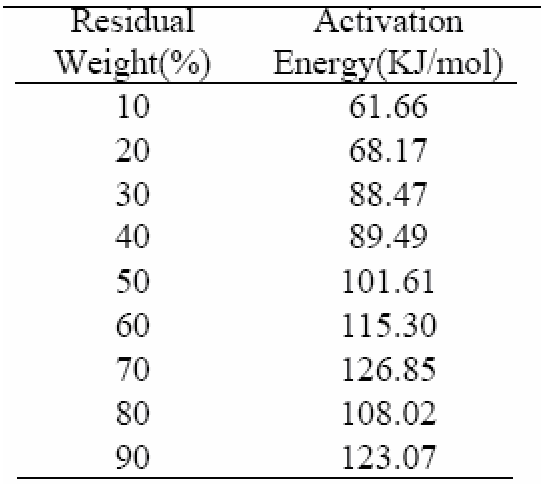
Fig. 8. TG curves of PE/Silica-Alumina at various heating rate. Heating rate –♦–1.5 K/min, –■–2 K/min K, –▲–2.5 K/min.

Table 9
The activation energies for PE/ X-Zeolite at different mass fraction.



Residual Weight(%)	Activation Energy(KJ/mol)
10	87.93
20	88.08
30	85.65
40	79.44
50	65.43
60	63.93
70	70.27
80	73.15
90	65.11

Table 10
The activation energies for PE/ Silica-Alumina at different mass fraction.



Residual Weight(%)	Activation Energy(KJ/mol)
10	61.66
20	68.17
30	88.47
40	89.49
50	101.61
60	115.30
70	126.85
80	108.02
90	123.07

4.4.4. Determination of reaction order with respect to catalyst

By taking the natural logarithm of right and left hand sides of the Eq. (12) we get $LnR = Lnk' + \beta Ln[Cat]$ where R is degradation rate, k' is apparent rate constant and [Cat] is concentration of catalyst.

The plots of LnR vs. $ln[Cat]$ are linear and plotted in Figs. 9 and 10 for X-Zeolite and Silica-Alumina respectively. The results are shown in these figures carried out with 0.25 g of polymer and different concentration of catalyst (0.02, 0.03, 0.04 and 0.05 g) at 370 ºC. The slopes of the line (reaction order) are 0.69 and 0.14, for X-Zeolite and Silica-Alumina respectively.

4.4.5. To compare effect of catalyst

To study and to compare action of catalysts on degradation of PE, we degraded pure PE and PE with X-Zeolite and Silica-Alumina at 370ºC and calculated percent of conversion. Data of the degradation are shown in Fig.11. As indicated by this figure, the extent of degradation with catalyst gradually increased. According to result that presented in Fig. 11 it was found that X-Zeolite has most percent of conversion, In other hand, with comparing activation energies it has found that X-Zeolite decrease activation energy of degradation reaction more than Silica-Alumina. Therefore this catalyst has most rate of degradation.

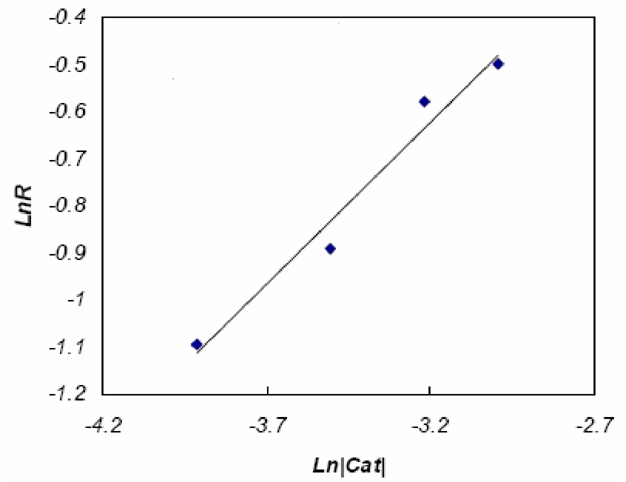


Fig. 9. Plots of LnR versus Ln |cat| for the thermal degradation for PE/ X-Zeolite.

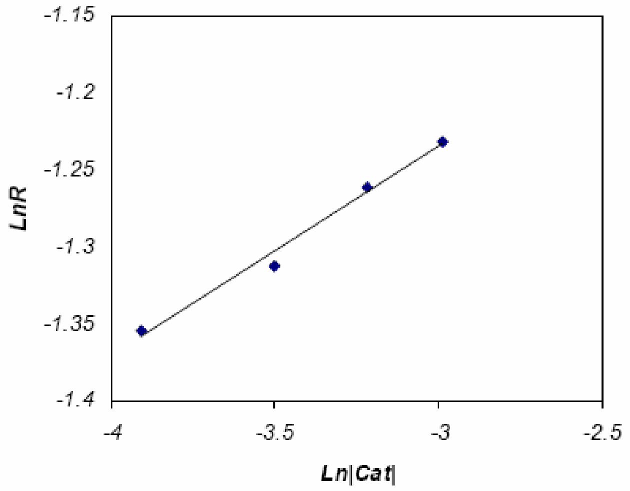


Fig. 10. Plots of LnR versus Ln |cat| for the thermal degradation for PE/ Silica-Alumina.

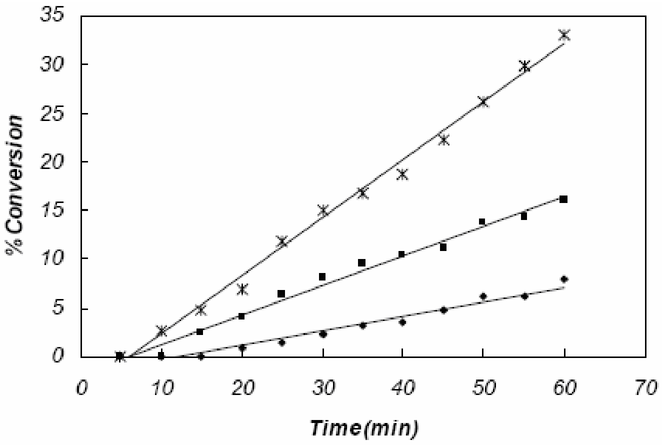


Fig. 11. Curves of percent of conversion versus time for thermal degradation. —◆—PE, —■— PE/ Silica-Alumina, —*— PE/ X-Zeolite.

5. Conclusions

The thermal degradation kinetics of pure PE and PE/Catalyst were studied in isothermal and dynamic condition. The effect of catalyst and concentration of catalyst on the thermal degradation has been studied. It was found that thermal degradation in presence to catalyst is more than pure polymer. Tendency of thermal degradation of samples as can be seen in order:

PE < PE/ Silica-Alumina < PE/X-Zeolite

Activation energy for thermal degradation was defined by using Arrhenius equation and Ozawa method which were Ea= 131.1 kJ mol^{-1} and 128.43 kJ mol^{-1} for pure PP, in isothermal and dynamic condition, respectively. The results showed that activation energy is different in every condition. However further studies should be carried out to investigate the role of the experimental conditions and to elucidate the reaction mechanism. With comparing activation energies in presence and absence of catalyst, it has found that catalyst decrease activation energy of degradation reaction and among two catalysts, X-Zeolite decrease activation energy more than Silica-Alumina. Therefore this catalyst has most rate of degradation.

References

[1] R. Chandra, R. Rustgi, Prog. Polym. Sci. 23 (1998) 1273-1335.

[2] R.W.J. Westerhout, J. Waanders, J.A.M. Kuipers, W.P.M. van Swaaij, Ind. Eng. Chem. Res. 36 (1997) 1955-1964.

[3] H. Bockhorn, A. Hornung, U. Hornung, D. Schawaller, J. Anal. Appl. Pyrolysis. 48 (1999) 93-109.

[4] H. Bockhorn, A. Hornung, U. Hornung, J. Anal. Appl. Pyrolysis. 50 (1999) 77-101.

[5] C.H. Wu, C.Y. Chang, J.L. Hor, S.M. Shih, L.W. Chen, F.W. Chang, Waste Management. 13 (1993) 221-235.

[6] G. Manos, A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 39 (2000) 1203-1208.

[7] G. Manos, A. Garforth, J. Dwyer, Ind. Eng. Chem. Res. 39 (2000) 1198-1202.

[8] G. Manos, Y.I. Yusof, N. Papayannakos, H.N. Gangas, Ind. Eng. Chem. Res. 40 (2001) 2220-2225.

[9] G. Manos, Y.I. Yusof, N. Papayannakos, H.N. Gangas, Energy Fuels. 16 (2002) 485-489.

[10] K. Gobin, G. Manos, Polym. Degrad. Stab. 83 (2004) 267-279.

[11] D.W. Park, E.Y. Hwang, J.R. Kim, J.K. Choi, Y.A. Kim, H.C Woo. Polym. Degrad. Stab. 65 (1999) 193-198.

[12] J.M. Arandes, J. Erena, M.J. Azkoiti, D. Lopez-Valerio, J. Bilbao, Fuel Processing Technology. 85 (2004) 125-140.

[13] H. Ohkita, R. Nishiyama, Y. Tochihara, T. Mizushima, N. Kakuta, Y. Morioka, A. Ueno, Y. Namiki, S. Tanifuji, H. Katoh, H. Sunazyka, R. Nakayama, T. Kuroyanagi, Ind. Eng. Chem. Res. 32 (1993) 3112-3116.

[14] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Applied. Catalysis B Environmental. 2 (1993) 153-164.

[15] J. Arguado, J.L. Sotelo, D.P. Serrano, J.A. Calles, J.M. Escola, Energy Fuels. 11 (1997) 1225-1231.

[16] R.C. Mordi. R. Field, J. Dwyer, J. Anal. Appl. Pyrolysis. 29 (1994) 45-55.

[17] W.C. McCaffrey, M.R. Kamal, D.G. Cooper. Polym. Degrad. Stab. 47 (1995) 133-139.

[18] K.Gobin, G. Manos. Polym. Degrad. Stab. 86 (2004) 225-231.

[19] G.J.T. Fernandes, V.J. Fernandes, Jr., A.S. Araujo. Catalysis Today 75 (2002) 233-238.

[20] L. B. Pierella, S. Renzini, O.A. Anunziata, Microporous and Mesoporous Materials 81 (2005) 155-159.

[21] J.I. Won Park, J.H. Kim, G. Seo, Polym Degrad Stab. 76 (2002) 495-501.

[22] I.C. Neves, G. Botelho, A.V. Machadob, P. Rebelo. Materials Chemistry and Physics 104 (2007) 5-9.

[23] K. Gobin, G. Manos. Polym. Degrad. Stab. 83 (2004) 267-279.

[24] A. Durmuş, S. Naci Koç, G. Selda Pozan, A. Kaşgöz, Applied Catalysis B: Environmental. 61 (2005) 316-322.

[25] C. D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639-642.

[26] A. Marcilla, R. Ruiz-Femenia, J. Hernandes, J. Anal. Appl. Pyrolysis. 76 (2006) 254-259.