

Kinetic Analysis for the Catalytic Pyrolysis of Polyethylene Terephthalate Over Cost Effective Natural Catalysts

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Abstract

In the current research, thermal and catalytic thermogravimetric (TG) analysis of polyethylene terephthalate (PET) over natural zeolite (NZ), olivine, bentonite, HZSM-5, and HAI-MCM-41 were investigated using a TG analyzer and model-free kinetic analysis. Catalytic TG analysis of PET was carried out at multi-heating rates, 10, 20, 30, and 40 °C/min, under nitrogen atmosphere. Apparent activation energy (Ea) values for the thermal and catalytic pyrolysis of PET were calculated using Flynn-Wall-Ozawa method. Although natural catalysts, NZ, olivine, and bentonite, could not lead the higher PET decomposition efficiency than synthetic zeolites, HZSM-5 and HAI-MCM-41, maximum decomposition temperatures on the differential TG (DTG) curves for the catalytic pyrolysis of PET, 436 °C over olivine, 435 °C over bentonite, and 434 °C over NZ, at 10 °C/min, were definitely lower than non-catalytic pyrolysis. Calculated Ea values for the catalytic pyrolysis of PET over natural catalysts, 177 kJ/mol over olivine, 168 kJ/mol over bentonite, and 171 kJ/mol over NZ, were also not lower than those over synthetic zeolites, however, those were also much lower than the thermal decomposition, suggesting their feasibility as the proper and cost-effective catalysts on the pyrolysis of PET.

Keywords: Polyethylene terephthalate, Kinetic analysis, Bentonite, Pyrolysis

1. Introduction

Polyethylene terephthalate (PET) is known as a common plastic widely used in many industries, such as textile, carpet, packaging, films, and fibers manufacturing[1,2]. Owing to its proper physicochemical properties, the overall production amount of PET has increased dramatically in recent years. The amount of waste PET bottle is also increased rapidly and the government reinforced the recycling policy of PET with proper guideline. Owing to these policies and technical development, the successful recycling process is enlarged with the larger amount of facility investigation[3]. Although PET bottle can be properly recycled, the considerable amount of PET wastes is still difficult to be recycled due to the co-presence of impurities, pigment, and so on, with PET[4]. Pyrolysis can be the proper solution to increase the recycling efficiency of PET because the large amount of chemical and/or fuel can be produced from PET wastes containing other impurities[5]. Although the large amount of PET pyrolysis oil can be obtained by the simple pyrolysis, the high content of acids, such as benzoic acid, vinyloxy carbonyl benzoic acid, and biphenyl-4-carbox-

ylic acid, in PET pyrolysis oil is being considered as the limitation on the commercialization of PET pyrolysis process because high acidity of PET pyrolysis oil can cause the damage of plant utilities[6]. To overcome this limitation, the catalytic pyrolysis of PET was intensively investigated by many researchers. Kumagai *et al.*[7] used basic CaO for the formation of aromatic hydrocarbons by increasing the decarboxylation of acidic PET pyrolyzates. Park *et al.*[8] suggested the combined use of CaO and HZSM-5 to provide the cost effectiveness of the process and the maximized yield of aromatic hydrocarbons. Recently, they also reported that waste concrete also can provide the catalytic effect on the pyrolysis of PET due to its high CaO content. These findings can suggest the potential use of low-cost catalysts like natural minerals on the pyrolysis of PET. Ro *et al.*[9] suggested low-cost catalysts, such as bentonite and olivine, as cost-effective solution which can provide the catalytic cracking efficiency and decrease the catalyst cost on the catalytic pyrolysis of biomass. Although these catalysts can be considered as potential catalysts for the decomposition of PET, its actual approach was not reported, yet.

The feasibility of catalyst on the decomposition of organic solids can be evaluated by kinetic analysis and/or reaction product comparison [10-15]. Kinetic analysis is important because suitable pyrolysis reactor design can be achieved by understanding solid decomposition kinetics. The change of kinetic parameters, such as apparent activation energy (Ea), pre-exponential factor, and reaction model, can be achieved by the proper catalyst use. Kang *et al.*[16] reported that Ea values for PET

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decomposition over acid zeolites were much lower than non-catalytic reaction.

In this study, kinetic analysis for the thermal and catalytic pyrolysis of PET was performed using a TG and model-free kinetic analysis. Catalytic TG analysis was performed by heating PET or PET and catalyst mixture at multi-heating rates under nitrogen atmosphere. Flynn-Wall-Ozawa[17] model (FWO) was applied to calculate Ea values on the thermal and catalytic pyrolysis of PET without the assumption of reaction model.

2. Experimental

2.1. PET and Catalysts

Polyethylene terephthalate (PET) having its particle size smaller than 300 μm was purchased from Goodfellow. Table 1 shows proximate analysis of PET. HZSM-5, HAI-MCM-41, and bentonite were purchased from Zeolyst, ACS material, and Sigma Aldrich, respectively. Olivine and NZ were obtained from a local supplier in Korea. All the catalysts were calcined at 500 $^{\circ}\text{C}$ for 3 hours prior to TG analysis.

Table 1. Proximate Analysis of PET

Proximate Analysis (dry basis)	wt. %
Volatile	93.5
Fixed Carbon	6.5
Ash	-
Sum	100

2.2. Kinetic analysis

1 mg of PET or 2 mg of PET and catalyst mixture (1/1) were heated from 40 $^{\circ}\text{C}$ to 750 $^{\circ}\text{C}$ at 10, 20, 30 and 40 $^{\circ}\text{C}/\text{min}$ under 50 mL/min of N_2 atmosphere in a TG analyzer (Pyris 1, Perkin Elmer).

FWO was used in order to calculate activation energy in this study. Briefly, the kinetic equation can be obtained according to below procedures.

Conversion rate (X) of PET can be calculated using Equation 1:

$$X = (m_0 - m) / m_0 - m_f \quad (1)$$

Where m, m_0 , and m_f are instantaneous, initial and final mass, respectively. On the other hand, the rate of conversion was calculated using following formula (Equation 2):

$$dX/dt = kf(X) \quad (2)$$

Where k and f(X) are the rate constant and the reaction model function, respectively. Meanwhile, k is expressed by Arrhenius Law and describes as follows (Equation 3):

$$k(T) = A_0 \exp.(-E_a/RT) \quad (3)$$

Where A_0 is pre-exponential factor (min^{-1}), E_a is activation energy

(kJ/mol), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). Using Equation 3, Equation 2 could be written as Equation (4):

$$d\alpha/dt = A_0 \exp.(-E_a/RT)f(X) \quad (4)$$

By introducing the heating rate ($\beta = dT/dt$) and applying a simple integration of Equation (4), Equation (5) can be obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (5)$$

Where $g(\alpha)$ is the conversion function of the kinetic decomposition of PET at a specified heating rate. The FWO method based on Doyle's approximation can be applied to resolve the Equation (5) which results Equation (6):

$$\ln(\beta) = \ln[A_0 E_a / R f(X)] - 5.331 - 1.052 E_a / RT \quad (6)$$

Furthermore, in this method, E_a values for each conversion rate can be determined by calculating the slop of $\ln(\beta)$ versus $1/T$ plot.

3. Results and discussion

TG and derivative TG (DTG) curves for the thermal and catalytic pyrolysis of PET at 10 $^{\circ}\text{C}/\text{min}$ were shown in Figure 1. Thermal TG analysis of PET had a sharp DTG curve, suggesting the single decomposition of PET. Martin-Gullon *et al.*[18] explain that the thermal degradation of PET starts by random chain scission at the ester linkage and leads the formation of carboxyl and vinyl ester groups. Then this scission undergoes many different gaseous substances (primary products), and continues reacting among themselves (or air, in case of using air as the gas flow) which produce secondary products. They also suggested that PET decomposition initiates at the higher temperature than 300 $^{\circ}\text{C}$ due to its high thermal stability, as shown at 333 $^{\circ}\text{C}$ in our result (Figure 1). In addition, Zhang[19] observed that PET degradation started at temperature of 375 $^{\circ}\text{C}$ and continued to 550 $^{\circ}\text{C}$.

The catalytic TG analysis of PET over the catalysts also initiated PET decomposition at similar temperature between 340 $^{\circ}\text{C}$ and 350 $^{\circ}\text{C}$. Meanwhile, the decomposition rate (dX/dT) of PET over HZSM-5 was rapidly increased compared to thermal decomposition and other catalytic pyrolysis. Meanwhile, maximum decomposition temperatures (T_{max}) on the DTG curves for the thermal and catalytic pyrolysis of PET were different depending on the catalyst. All catalysts revealed lower T_{max} compared to non-catalytic reaction. T_{max} (438 $^{\circ}\text{C}$) obtained on the non-catalytic TG analysis was lowered to 435 $^{\circ}\text{C}$ by the use of bentonite, 434 $^{\circ}\text{C}$ by NZ, and 436 $^{\circ}\text{C}$ by olivine, respectively. Synthetic zeolites shifted T_{max} to the much lower temperatures, 422 $^{\circ}\text{C}$ over HZSM-5 and 427 $^{\circ}\text{C}$ over HAI-MCM-41, compared to natural catalysts.

Different PET decomposition efficiency of the catalysts can be explained by catalyst acidity and pore properties. Among natural catalysts

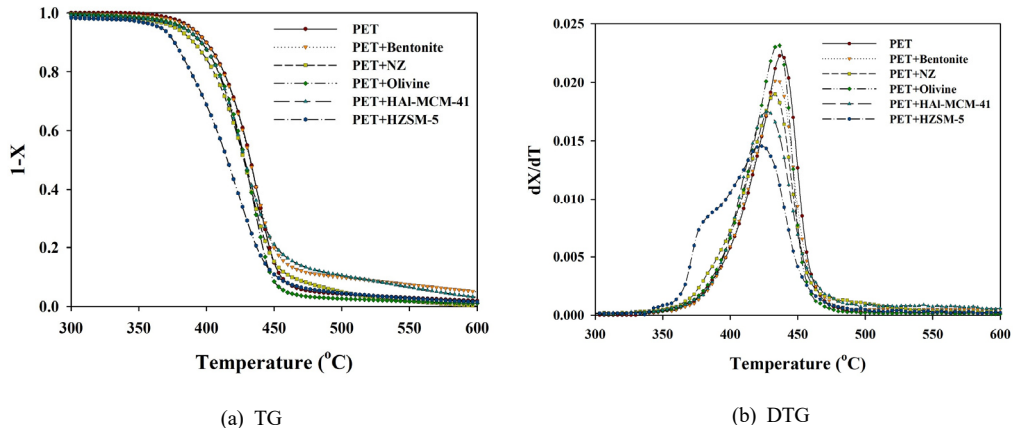


Figure 1. (a) TG and (b) DTG curves for the thermal and catalytic pyrolysis of PET at 10 °C/min.

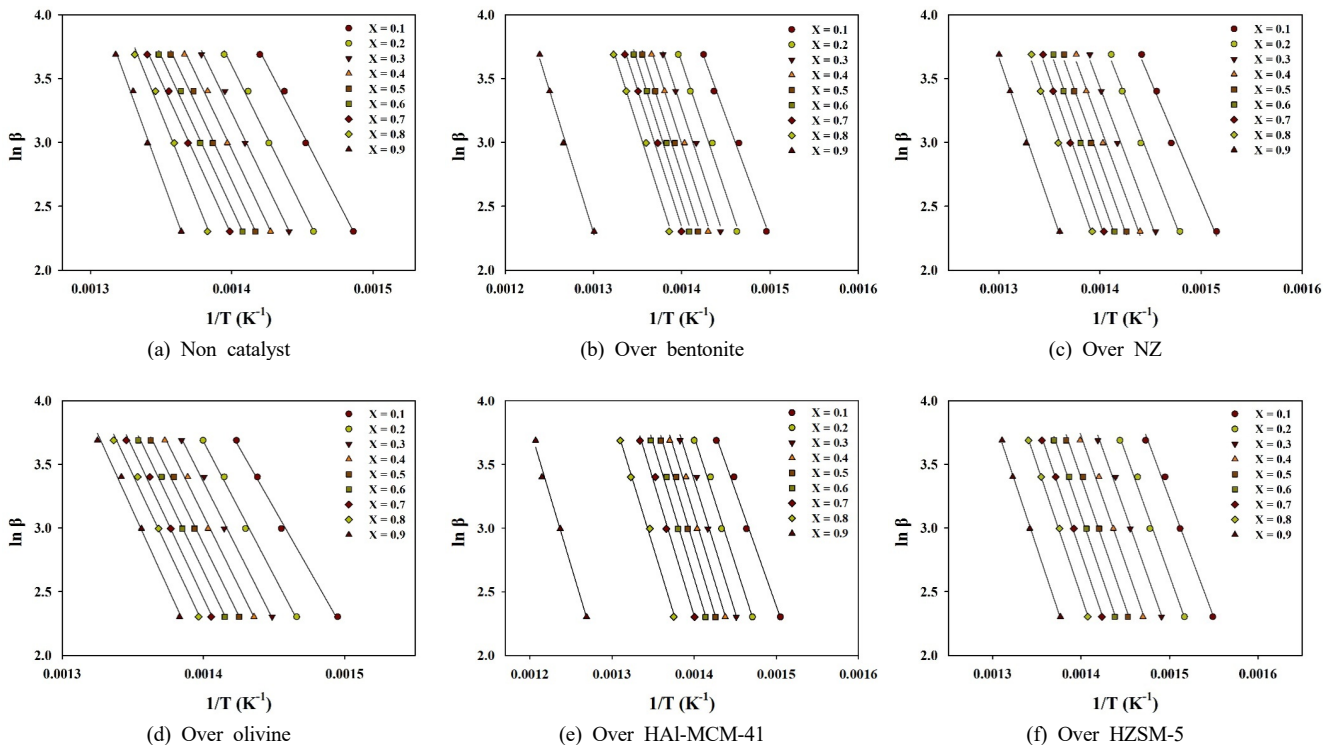


Figure 2. The plots of $\ln(\beta)$ versus $1/T$ at each conversion rate obtained from the thermal and catalytic TG analysis data of PET at 10, 20, 30, and 40 °C/min.

used in this study, bentonite and olivine have larger pore size, 29.8 nm and 7.9 nm respectively[9], than HZSM-5 (0.55 nm). NZ has the smallest pore size (0.5 nm) among the catalysts used in this study. These indicate that the diffusion limitation of reactant molecules to the pore of bentonite and olivine is lower than that of HZSM-5. Meanwhile, natural catalysts have the lower acidities around 400 °C, 0.122 mmol/g (bentonite), 0.151 mmol/g (NZ), and almost no acidity (olivine), than HAl-MCM-41 (0.553 mmol/g) and HZSM-5 (0.573 mmol/g). This suggests that the catalyst acidity is more important factor concluding PET decomposition rates. Park *et al.*[8] also claimed

that the larger amount of acid sites is an important factor lowering T_{\max} of PET.

Figure 2 shows the plots of $\ln(\beta)$ versus $1/T$ at each conversion rate obtained from the thermal and catalytic TG analysis data of PET. High linearity ($R^2 > 0.99$) on the plots indicates the properness of kinetic analysis applied in this study.

Figure 3 and Table 2 revealed E_a values for the thermal and catalytic pyrolysis of PET in each conversion. E_a values in all experimental cases were increased with the conversion increase. The sudden increase of E_a at the higher conversion than 0.7 on the thermal

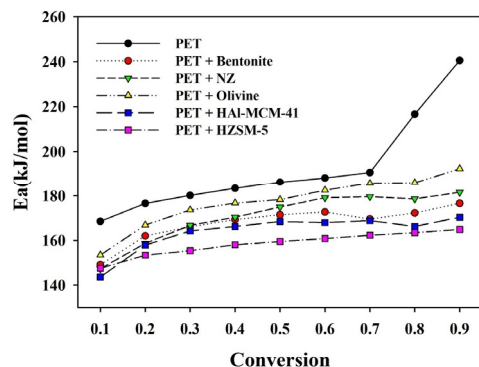


Figure 3. Activation energy values obtained from catalytic and non-catalytic TGA data.

pyrolysis of PET can be explained with the additional cracking of char intermediates. Although the catalytic pyrolysis of PET had the gradual increase of E_a , sudden E_a increase at higher conversion was not monitored. Among the catalysts, the catalytic pyrolysis of PET over HZSM-5 had the lowest E_a value (158 kJ/mol), followed in order by that over HAI-MCM-41 (164 kJ/mol), bentonite (168 kJ/mol), NZ (171 kJ/mol), and olivine (177 kJ/mol). These results can be explained with the high acidity of HZSM-5 and HAI-MCM-41. While NZ had more

acid sites than bentonite, the small pore size of NZ can hinder the diffusion of PET molecules. It is meaningful that the catalytic pyrolysis of PET over bentonite, one of the natural catalysts having proper pore size and acidity, displayed similar E_a values with those over synthetic zeolites because the use of natural catalysts can largely decrease the catalyst cost on the actual commercialization.

4. Conclusion

Kinetic analysis for the catalytic pyrolysis of PET over bentonite, NZ, and olivine suggested the feasibility of natural catalysts for increasing PET pyrolysis efficiency and process cost effectiveness in this study. From TG and DTG analysis results, T_{max} on the non-catalytic pyrolysis of PET was 438 °C. T_{max} is lowered to 435 °C over bentonite, 434 °C over NZ, and 436 °C over olivine, respectively, by using natural catalysts. While using synthetic zeolites, T_{max} became much lower, 422 °C over HZSM-5 and 427 °C over HAI-MCM-41, compared to natural catalysts. The E_a value on the pyrolysis of PET was calculated (192 kJ/mol) by using FWO method. In the same way, E_a values for the catalytic pyrolysis of PET over different catalysts were revealed as follows, 168 kJ/mol over bentonite, 171 kJ/mol over NZ, 177 kJ/mol over olivine, 164 kJ/mol over HAI-MCM-41, and 158 kJ/mol over HZSM-5. Although natural catalysts could not reveal high-

Table 2. Activation Energy (E_a) and Coefficient of Determination (R^2) Values at Each Conversion

X	PET		PET + Bentonite		PET + NZ	
	E_a	R^2	E_a	R^2	E_a	R^2
0.1	168.5	0.996	149.1	0.991	147.4	0.986
0.2	176.6	0.996	162.0	0.991	158.7	0.994
0.3	180.1	0.995	166.1	0.992	166.7	0.992
0.4	183.4	0.995	169.3	0.992	170.4	0.991
0.5	186.3	0.995	171.5	0.992	174.9	0.994
0.6	188.2	0.996	172.7	0.990	179.1	0.996
0.7	190.7	0.996	169.6	0.992	179.6	0.996
0.8	216.7	0.993	172.3	0.992	178.6	0.994
0.9	240.5	0.995	176.6	0.995	181.5	0.997
Average	192.3	0.995	167.7	0.992	170.8	0.993

X	PET + Olivine		PET + HAI-MCM-41		PET + HZSM-5	
	E_a	R^2	E_a	R^2	E_a	R^2
0.1	153.4	0.996	143.6	0.991	147.5	0.992
0.2	166.9	0.996	157.9	0.991	153.4	0.991
0.3	173.6	0.996	164.2	0.990	155.4	0.994
0.4	176.7	0.996	166.2	0.990	158.0	0.991
0.5	178.2	0.996	168.5	0.992	159.5	0.995
0.6	182.5	0.996	168.0	0.991	160.8	0.997
0.7	185.7	0.995	168.9	0.992	162.3	0.999
0.8	186.0	0.994	166.2	0.996	163.4	0.999
0.9	192.3	0.992	170.4	0.993	164.9	0.999
Average	177.3	0.995	163.7	0.992	158.3	0.995

er performance on decreasing the T_{\max} and E_a values than synthetic zeolites, they also revealed the catalytic effect on PET decomposition. Among three natural catalysts, bentonite led the lowest T_{\max} and E_a values on PET decomposition, comparable with the effect of HAI-MCM-41.

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