

# COMBUSTION KINETICS OF POLYETHYLENE TEREPHTHALATE

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**Abstract** : The combustion kinetics of poly(ethylene terephthalate) (PET) was studied by the dynamic model which accounts for the thermal decomposition of polymer at any time. The kinetic analysis was performed by a conventional nonisothermal thermogravimetric (TG) technique at several heating rates between 10 and 40 K/min in air atmosphere. The thermal decomposition of PET in air atmosphere was found to be a complex process composed of at least two stages for which kinetic values can be calculated. The combustion kinetic analysis of PET gave apparent activation energy for the first stage of 257.3~269.9 kJ/mol, with a value of 140.5~213.8 kJ/mol for the second stage. To verify the effectiveness of the kinetic analysis method used in this work, the kinetic analysis results were compared with those of various analytical methods. The kinetic parameters were also compared with values of the pyrolysis of PET in nitrogen atmosphere.

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**Key Words** : Combustion Kinetics, Poly(ethylene terephthalate), Thermogravimetric technique

## INTRODUCTION

In recent years, as quantities of municipal and industrial organic waste increase, the thermal treatment of solid wastes has received considerable attention. A proper thermal treatment system not only resolves the disposal problems, but also recovers energy from these wastes. Particularly, the high-temperature incineration process such as rotary kiln can affect the total conversion of organic waste to safe, innocuous, thermodynamically controlled, end-products, such as carbon dioxide and water.<sup>1,2)</sup> Organic wastes are subjected to thermal decomposition in solid feed to incinerator and so, the thermal decomposition kinetics of organic waste must be studied to provide a more detailed thermal

and flow analysis<sup>3-6)</sup>. This will permit development of an optimum process at an ideal level. Thermogravimetric analysis (TG) can't be used to elucidate clear mechanism of thermal decomposition of polymer. Nevertheless, much effort has been devoted to develop a new mathematical method for kinetic analysis using TG because it gives reliable information on the apparent activation energy and the overall reaction order<sup>7-11)</sup>.

In this work the combustion kinetics of PET was studied by the kinetic analysis method developed in our previous work<sup>12)</sup>. This work focuses on the apparent kinetic parameters useful for chemical engineering design. The actual values of kinetic parameters obtained by using a conventional thermogravimetric technique are dependent not only on such factors as atmosphere, sample mass, sample shape, flow rate, heating rate, etc., but also upon the

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mathematical treatment used to evaluate the data. In their studies of the kinetic analysis of thermogravimetric data for the pyrolysis of styrene-butadiene rubber, Oh et al.<sup>13)</sup> presented there were tremendous variations depending upon the mathematical approach taken in the analysis.<sup>13)</sup> Therefore, to verify the effectiveness of the kinetic analysis method used in this work, the kinetic analysis results were compared with those of various analytical methods.

## EXPERIMENT

The combustion kinetics of PET for non-isothermal conditions has been investigated thermogravimetrically. The PET samples were obtained from KP Chemical Co., Ltd., Korea, and used without further treatment. The experiments were carried out for various heating rates (10, 20, 30 and 40 K/min) in air and nitrogen atmosphere with a flow rate of 50 ml/min and a purge time 20 min. The initial mass of the sample was 27~35 mg. The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. It consists of an electrically heated reaction tube (18 mm i.d. and 165 mm in length). The sample was placed in a quartz cell of 6 mm in diameter. The cell was then put on a platinum crucible connected to the thermobalance. Carrier gas was supplied from a gas bottle and regulated by a mass flow meter. The gas passed through the reaction tube from top to bottom. The variation of the sample mass with reaction temperature was detected by a photoelectric element and weight-measuring circuits in the thermobalance.

## KINETIC ANALYSIS

### Kinetic Model

In general, the overall rate equation of conversion  $\alpha$  for thermal decomposition is expressed in Arrhenius form as

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp(-E/RT) \quad (1)$$

$A$  is not strictly constant but depends, based on collision theory<sup>14)</sup>, on  $T^{1/2}$ . If the heating rate  $\beta = dT/dt$  is employed, it can be shown that

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^{1/2} (1-\alpha)^n \exp(-E/RT) \quad (2)$$

By differentiation of Eq. (2),

$$\frac{d^2\alpha}{dT^2} = \frac{1}{\beta} \left( \frac{d\alpha}{dT} \right) \left[ n(1-\alpha)^{-1} \left( -\frac{d\alpha}{dT} \right) + \frac{E}{RT^2} + \frac{1}{2} T^{-1} \right] \quad (3)$$

From Eqs. (2) and (3), we can obtain the following expressions for  $E$  and  $n$ .

$$E = -RT \ln \left[ \frac{\left( \frac{d\alpha}{dT} \right)}{A_0 T^{1/2} (1-\alpha)^n} \right] \quad (4)$$

$$n = \frac{\left[ \left( \frac{d^2\alpha}{dT^2} \right) \left( \frac{d\alpha}{dT} \right) - \frac{E}{RT^2} - \frac{1}{2} T^{-1} \right] (1-\alpha)}{\left( -\frac{d\alpha}{dT} \right)} \quad (5)$$

We can easily obtain the values of  $d^2\alpha/dT^2$  and  $d\alpha/dT$  from TG data. Therefore, if the factor  $A_0$  is determined, the  $n$  and  $E$  values at any weight loss fraction can be obtained from Eqs. (4), (5) and TG data by numerical method.

### Determination of Factor, $A_0$

From Eq. (2), it can be shown that

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A_0}{\beta} T^{1/2} \exp(-E/RT) dT \quad (6)$$

where on integrating and introducing the initial condition of  $\alpha = 0$  at  $T = T_0$  the following expression is obtained as

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A_0}{\beta} \int_{T_0}^T T^{1/2} \exp(-E/RT) dT \quad (7)$$

The integral approximation<sup>15)</sup> is to consider Eq. (7) when it can be shown that

$$\begin{aligned} & \frac{A_0}{\beta} \int_{T_0}^T T^{1/2} \exp(-E/RT) dT \\ & = \frac{A_0 R}{\beta E} T^{5/2} \left( 1 - \frac{5RT}{2E} \right) \exp(-E/RT) \end{aligned} \quad (8)$$

while

$$\int \frac{d\alpha}{(1-\alpha)^n} = \frac{1-(1-\alpha)^{1-n}}{1-n} \text{ for } n \neq 1 \quad (9)$$

Therefore, we can obtain that

$$\frac{1}{n-1} \left[ \frac{1}{(1-\alpha)^{n-1}} - 1 \right] = \frac{A_0 R}{\beta E} T^{5/2} \left( 1 - \frac{5RT}{2E} \right) \exp(-E/RT) \text{ for } n \neq 1 \quad (10)$$

Also, the maximum decomposition occurs when  $d^2\alpha/dT^2$  is zero. Therefore, Eq. (3) at maximum decomposition rate gives

$$\frac{A_0}{\beta} T_m^{1/2} \exp(-E_m/RT_m) n(1-\alpha_m)^{n-1} = \frac{E_m}{RT_m^2} + \frac{1}{2} T_m^{-1} \quad (11)$$

If Eq. (11) is combined with Eq. (10), the following result is obtained

$$n(1-\alpha_m)^{n-1} = n - (n-1) \left[ 1 - \frac{2RT_m}{E_m} - 5 \left( \frac{RT_m}{2E_m} \right)^2 \right] \approx 1 \quad (12)$$

since  $\left[ 1 - \frac{2RT_m}{E_m} - 5 \left( \frac{RT_m}{2E_m} \right)^2 \right] \approx 1$

The product  $n(1-\alpha_m)^{n-1}$  in Eq. (12) is nearly equal to unity. Also  $n(1-\alpha_m)^{n-1}$  is exactly equal to unity for  $n=1$ . By substituting this value in Eq. (11) and taking the natural logarithm, one obtains

$$\ln \beta = \ln A_0 + \frac{3}{2} \ln T_m - \ln \left( \frac{E_m}{RT_m} + \frac{1}{2} \right) - \frac{E_m}{RT_m} \quad (13)$$

The plot of  $\ln \beta$  versus  $1/T_m$  should give a straight line with the slope determining the activation energy  $E_m$  at maximum decomposition rate, and  $\ln A_0$  can be calculated from the activation energy  $E_m$  and the intercept of the Y axis.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the variations of the TG and DTG curves with respect to temperature for various heating rates in nitrogen and air atmosphere, respectively. It is seen from

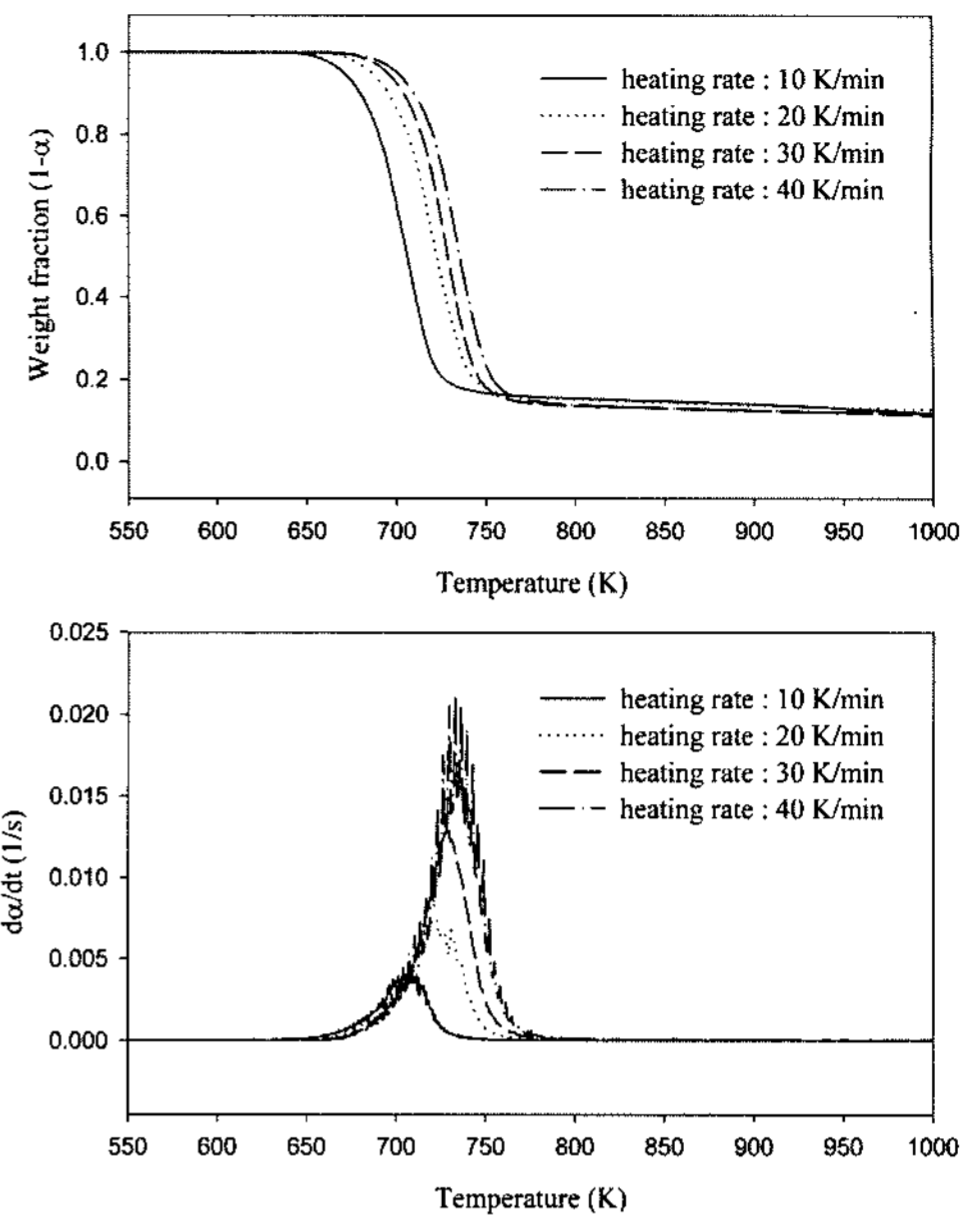


Figure 1. TG and DTG curves of PET in nitrogen atmosphere at various heating rates

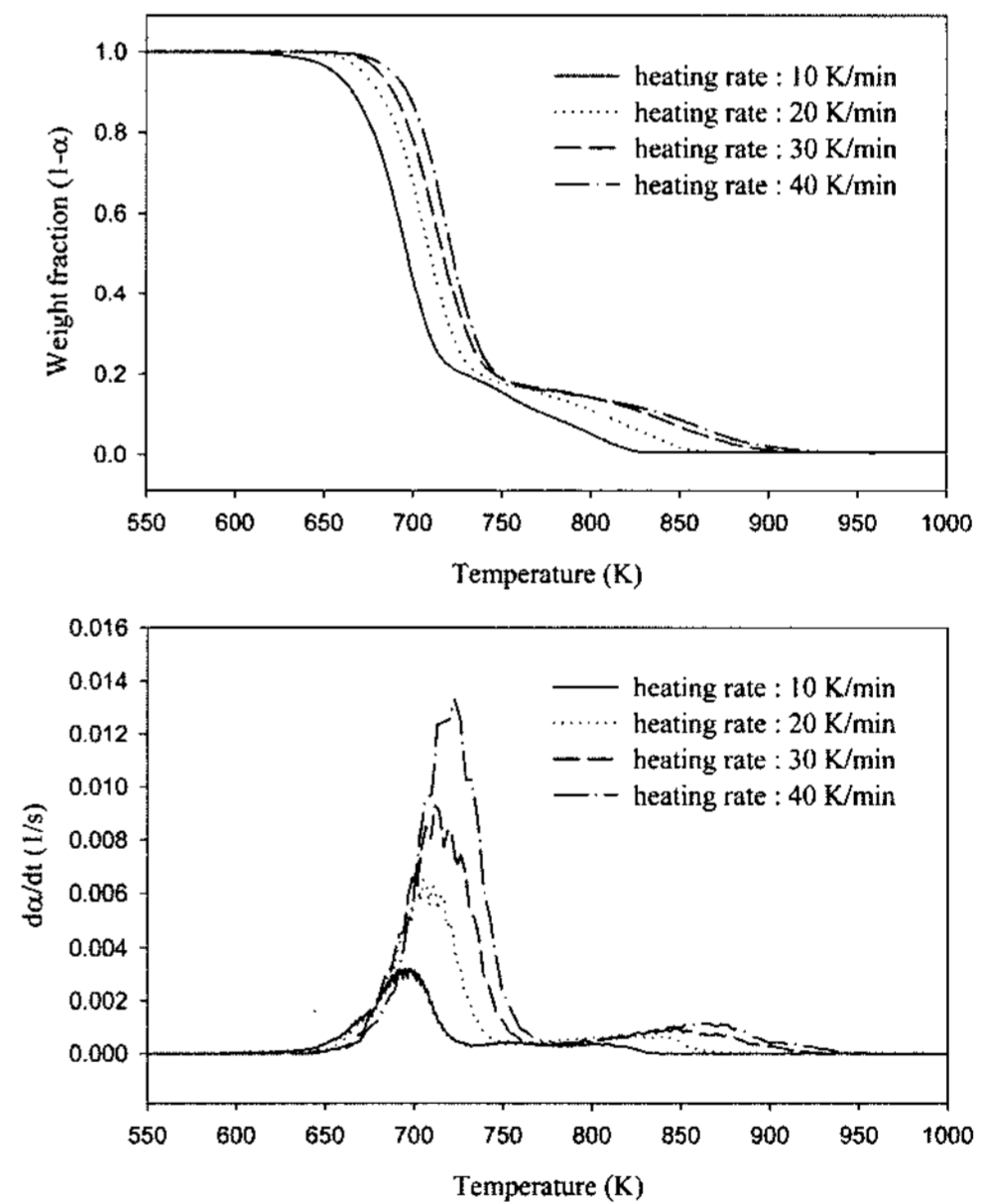


Figure 2. TG and DTG curves of PET in air atmosphere at various heating rates

Figures 1 and 2 that the TG curves are displaced to higher temperatures due to the heat transfer lag with increased heating rate and the height of the DTG peaks increases with the heating rate, which is in good agreement with Chen and Yeh.<sup>4)</sup> From Figure 1., it is found

that DTG curve for heating rate of 40 K/min are not smooth. Those phenomena were also found in our previous work.<sup>12,13)</sup> Therefore, it is felt that thermogravimetric phenomena at heating rate of 40 K/min are occurred by electric noise. There is just one peak in the DTG curve for each heating rate, which implies that only one kind of reaction occurs in nitrogen atmosphere. It is also observed that the residual mass fractions remain constant after 800 K for all four heating rates. The final residual mass fractions are about 0.09~0.11 for the heating rates of 10~40 K/min. It is seen from Figure 2 in air atmosphere that in contrast with the nitrogen atmosphere case, each TG curve has one additional plateau. There is one more point of inflection at a higher temperature ( $T \geq 800 \sim 900$  K) and a higher conversion ( $\alpha \geq 0.8$ ). Thus, it is seen that there are two stages of reaction.

This may be due to the residual mass not yet decomposed during the 1<sup>st</sup> stage combustion which reacts with air at a higher temperature. About 80% of total mass is lost at the end of the first reaction, with the remainder being removed in the second reaction. Figure 3. shows the plot of  $1/T_m$  against  $\ln \beta$  to calculate the factor  $A_0$  in Eq. (13). The plot in this figure results in straight line with slope equal to  $-E_m/R$ , thus the activation energy  $E_m$  at maximum decomposition rate can be easily obtained. The values of  $A_0$  obtained by substituting this value of  $E_m$  back into the intercept of Y axis are summarized in Table 1. The activation energies and the overall reaction orders upon conversion obtained from  $A_0$  and Eqs. (4), (5) and TG data are shown in Figures 4 and 5. From Figure 4., the kinetic analysis

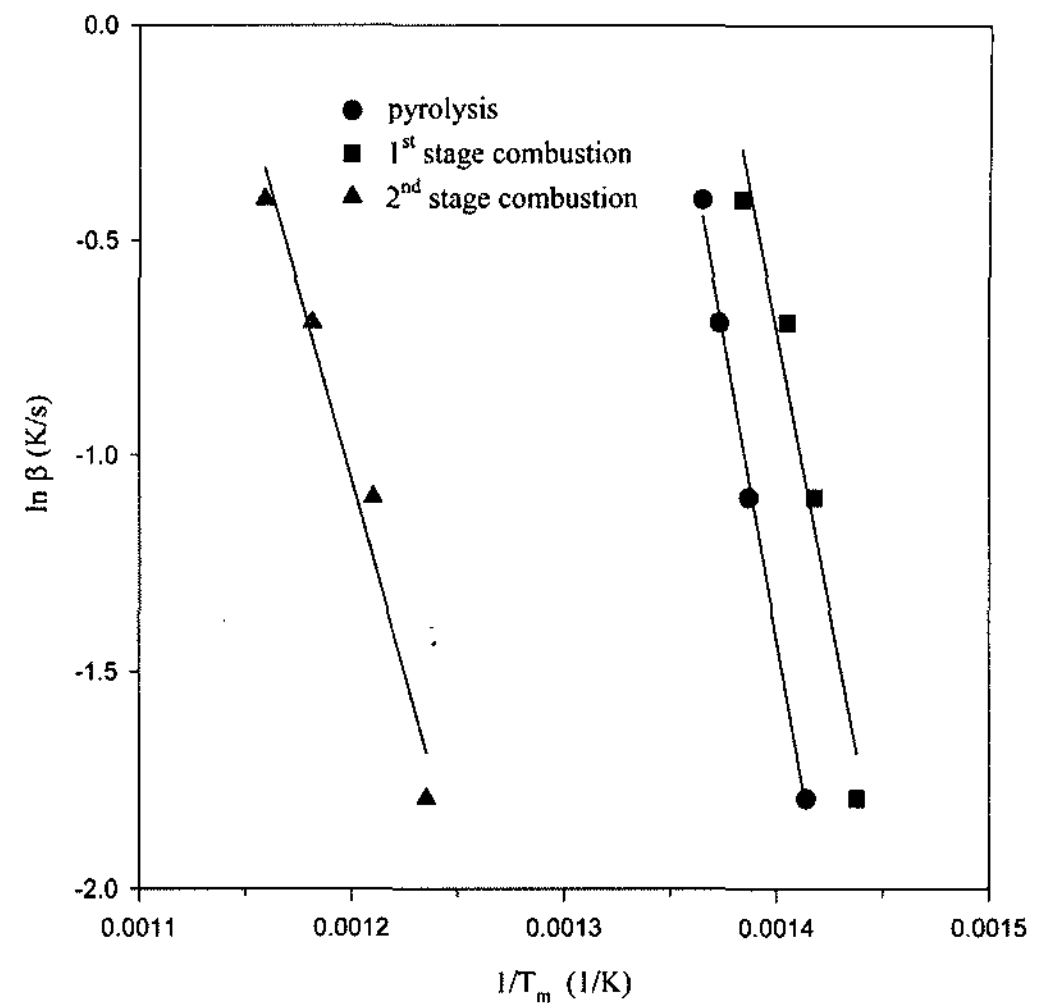
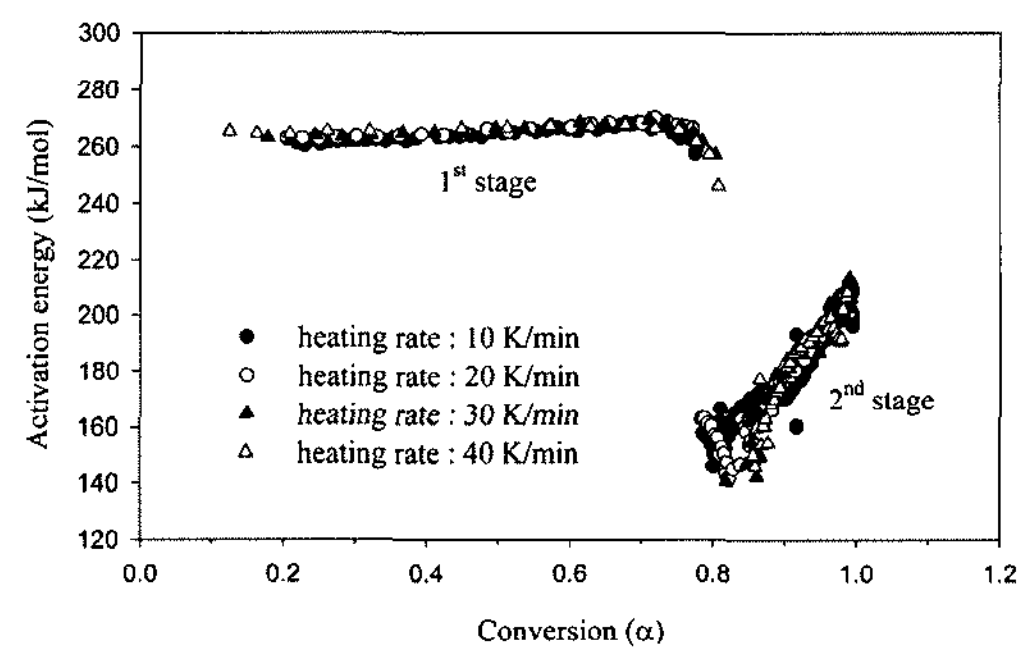
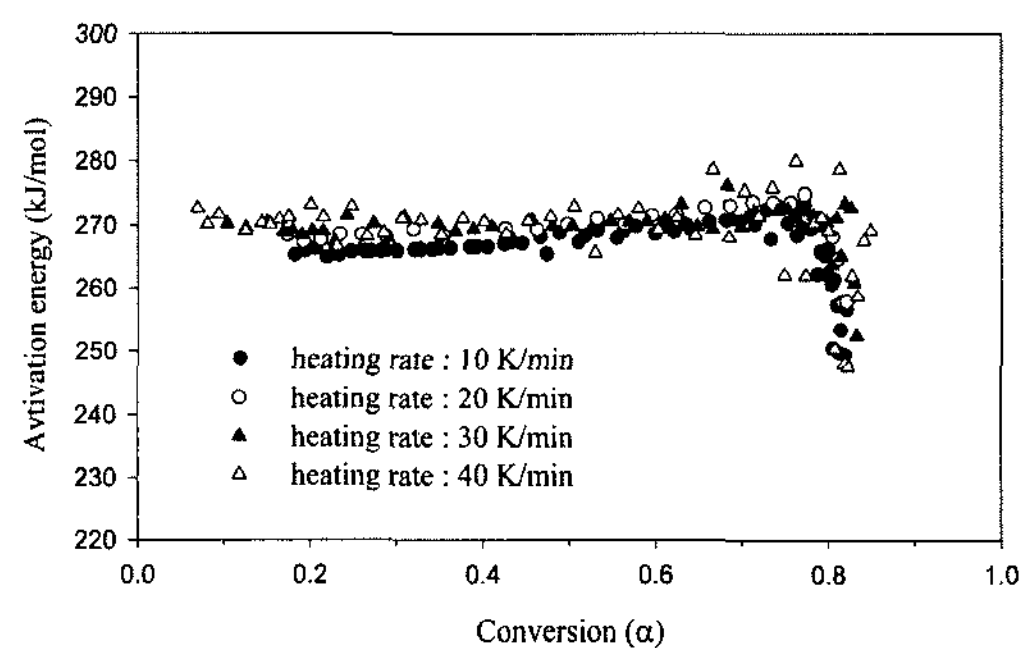


Figure 3. Plot of  $1/T_m$  vs.  $\ln \beta$  for the determination of factor  $A_0$



(a) Combustion



(b) Pyrolysis

Figure 4. Activation energy against conversion,  $\alpha$

Table 1. Determination of factor  $A_0$  in Eq. (2)

Heating rate (K/min)	Pyrolysis		1 <sup>st</sup> stage combustion		2 <sup>nd</sup> stage combustion	
	$E_m$ (kJ/mol)	$A_0$ (s <sup>-1</sup> K <sup>-1/2</sup> )	$E_m$ (kJ/mol)	$A_0$ (s <sup>-1</sup> K <sup>-1/2</sup> )	$E_m$ (kJ/mol)	$A_0$ (s <sup>-1</sup> K <sup>-1/2</sup> )
10	230.3	$2.5122 \times 10^{16}$	213.4	$2.7998 \times 10^{15}$	147.6	$4.8587 \times 10^8$
20		$2.4406 \times 10^{16}$		$2.7416 \times 10^{15}$		$4.7947 \times 10^8$
30		$2.4043 \times 10^{16}$		$2.7050 \times 10^{15}$		$4.7127 \times 10^8$
40		$2.3828 \times 10^{16}$		$2.6435 \times 10^{15}$		$4.4220 \times 10^8$

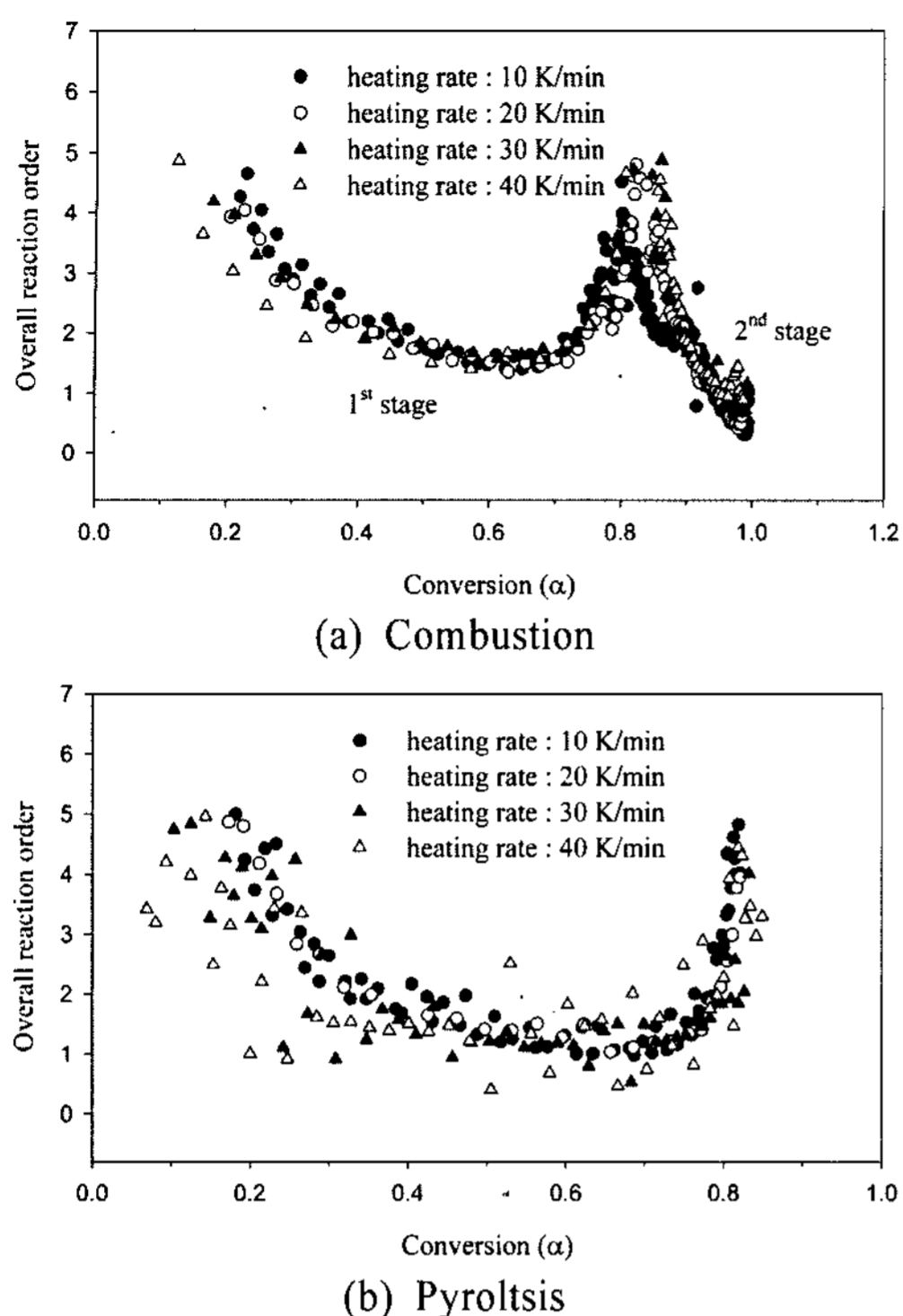


Figure 5. Overall reaction order against conversion,  $\alpha$ .

method used in this work gives the activation energies of 247.5~278.6 kJ/mol, 257.3~269.9 kJ/mol and 140.5~213.8 kJ/mol for the pyrolysis, 1<sup>st</sup> and 2<sup>nd</sup> stage combustion of PET, respectively. It is also found that the activation energies of 1<sup>st</sup> stage combustion are similar to those of pyrolysis, whereas the activation energies of 2<sup>nd</sup> stage combustion are lowered. It is seen that the activation energy is little affected by heating rates. Figure 5 shows the overall reaction order upon conversion. As can be seen in Figure 5, the multistages are clearly identified in air atmosphere. It is seen that the overall reaction orders are similar to those of pyrolysis and also little affected by heating rates.

Table 2 shows the comparison of the kinetic parameters results obtained from the various analytical methods reported in literatures.<sup>16-18)</sup> The kinetic parameters for multistage of PET combustion at any time are not obtained from the various analytical methods used in this

Table 2. Summary of the kinetic parameters used in the various analytical methods

Method	Pyrolysis		Combustion	
	Reaction order <i>n</i>	Activation energy <i>E</i> (kJ/mol)	Reaction order <i>n</i>	Activation energy <i>E</i> (kJ/mol)
Kissinger <sup>18)</sup>	1.0 <sup>a</sup>	217.4	1.0 <sup>a</sup>	191.0
Friedman <sup>16)</sup>	7.57	212.5 <sup>b</sup>	2.76	202.4 <sup>b</sup>
Ozawa <sup>18)</sup>	-	188.8 <sup>b</sup>	-	184.5 <sup>b</sup>
Flynn-Wall <sup>17)</sup>				
10 K/min	0.10	219.1	0.18	245.0
20 K/min	0.06	214.3	0.08	228.8
30 K/min	0.03	216.7	0.05	207.8
40 K/min	0.02	220.5	0.03	155.1
Chatterjee-Conrad <sup>18)</sup>				
10 K/min	1.0 <sup>a</sup>	273.5	1.0 <sup>a</sup>	212.8
20 K/min	1.0 <sup>a</sup>	263.5	1.0 <sup>a</sup>	252.6
30 K/min	1.0 <sup>a</sup>	302.7	1.0 <sup>a</sup>	274.2
40 K/min	1.0 <sup>a</sup>	308.6	1.0 <sup>a</sup>	270.5
Coats-Redfern <sup>15)</sup>				
10 K/min	1.0 <sup>a</sup>	278.5	1.0 <sup>a</sup>	189.9
20 K/min	1.0 <sup>a</sup>	286.3	1.0 <sup>a</sup>	225.4
30 K/min	1.0 <sup>a</sup>	316.4	1.0 <sup>a</sup>	249.6
40 K/min	1.0 <sup>a</sup>	311.1	1.0 <sup>a</sup>	267.8
This work				
10 K/min	2.31 <sup>b</sup>	266.2 <sup>b</sup>	2.06 <sup>b</sup>	221.7 <sup>b</sup>
20 K/min	2.30 <sup>b</sup>	269.3 <sup>b</sup>	2.11 <sup>b</sup>	221.4 <sup>b</sup>
30 K/min	2.10 <sup>b</sup>	269.6 <sup>b</sup>	2.18 <sup>b</sup>	225.0 <sup>b</sup>
40 K/min	2.25 <sup>b</sup>	268.9 <sup>b</sup>	2.26 <sup>b</sup>	223.4 <sup>b</sup>

<sup>a</sup> Assumed values, <sup>b</sup> Average values

work. Therefore, the activation energies and overall reaction orders from this work in Table 2 are shown as the average values. As can be seen in Table 2, there are tremendous variations in the calculated kinetic parameters depending upon the mathematical approach taken in the analysis. These observations clearly indicate the problems in the selection and utilization of different analytical methods to solve the thermal decomposition of PET. From Table 2, because of the wide variations with various heating rates in the calculated activation energies with the methods using the single heating rate experiments, it is felt that the best methods for analyzing the data are the methods using data collected at various heating rates such as Kissinger, Friedman and Ozawa methods. In their studies of the kinetic analysis of thermogravimetric data for the pyrolysis of PET, Cooney et al. concluded that the use of a multiple heating rate method was felt to represent more realistically the variety of heating rates for the thermal decomposition for polymer.<sup>18)</sup> However, Kissinger method uses the assumed value of 1.0 as the overall reaction order. Also, Ozawa method is only applicable to the calculation of activation energy and Friedman method can not give the overall reaction order of the thermal decomposition of PET at any time. While though the kinetic analysis used in this work uses the single heating rate experiments, the kinetic parameters for each heating rate can be obtained and the results are little affected by heating rates. Therefore, this method is capable of providing reasonably reliable data for the dynamic thermogravimetric analysis which accounts for the thermal decomposition of PET at any time.

## CONCLUSIONS

The combustion kinetics of PET was studied by the kinetic analysis method which accounts for the thermal decomposition of polymer at any time. From the comparison of the kinetic analysis results for the thermal decomposition of PET obtained from the various analytical methods, it was felt that the kinetic analysis

method proposed in this work was capable of providing reasonably reliable data for the dynamic thermogravimetric analysis which accounts for the thermal decomposition of PET at any time. The kinetic analysis using the various analytical methods showed tremendous variations depending upon the mathematical approach taken in the analysis. Because of the wide variations with various heating rates in a single heating rate technique, the use of a multiple heating rates technique was felt to represent more realistically the thermal decomposition of PET. However, though the kinetic analysis method used in this work uses the single heating rate experiments, the kinetic parameters are little affected by heating rates. From the kinetic analysis method used in this work, the apparent activation energies of the thermal decomposition of PET were calculated to be 247.5 ~ 278.6 kJ/mol, 257.3 ~ 269.9 kJ/mol and 140.5 ~ 213.8 kJ/mol for the pyrolysis, 1<sup>st</sup> and 2<sup>nd</sup> stage combustion of PET, respectively.

## NOMENCLATURE

- $A$  = pre-exponential factor ( $s^{-1}$ )
- $A_0$  = factor in Eq. (2) ( $s^{-1} K^{-1/2}$ )
- $E$  = apparent activation energy (J/mol)
- $E_m$  = apparent activation energy at maximum decomposition rate (J/mol)
- $n$  = overall reaction order, dimensionless
- $R$  = gas constant, 8.314 (J/mol K)
- $T$  = temperature (K)
- $T_m$  = temperature at maximum decomposition rate (K)
- $t$  = time (s)
- $\alpha$  = conversion, dimensionless
- $\alpha_m$  = conversion at maximum decomposition rate, dimensionless
- $\beta$  = constant heating rate (K/s)

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