Kinetics of Thermal Degradation of Waste Polypropylene and High-Density Polyethylene

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Abstract: A kinetic analysis of the thermal degradation of waste polypropylene (PP) and high-density polyethylene (HDPE) has been studied using a conventional thermogravimetric technique under a nitrogen atmosphere at several heating rates between 10 and 30 °C/min. To obtain the kinetic parameters to describe the thermal degradation of waste PP and HDPE, dynamic thermogravimetric analysis curves and their derivatives were analyzed using a variety of analytical methods. The waste PP and HDPE samples were obtained from a recycling center for waste plastics. Our results suggest that the best methods for the kinetic analyses of the thermal degradation of waste PP and HDPE are the Dynamic and Friedman methods. In addition, we found that the activation energy for a waste blend was smaller than those of waste PP and HDPE.

Keywords: thermal degradation, kinetics, waste PP, HDPE, thermogravimetric technique

Introduction

The amount of waste plastic is increasing continuously and this situation causes serious pollution problems. Because waste plastics are essentially non-biodegradable, they are not suitable either for composting or landfills. Accordingly, thermal treatment by pyrolysis or incineration is a more attractive alternative. Pyrolysis, which converts waste plastics to fuel or useful hydrocarbons, is recognized as a very useful approach. Uemura and coworkers [1] studied a pyrolysis reactor for the creation of a new plastic recycling process, but it was never commercialized because of lacking of economic, environmental, and political incentives on one hand and because of operational problems on the other. For the commercialization of such pyrolysis reactors, the kinetics of the thermal degradation of waste plastics must be analyzed to provide the apparent kinetic parameters that are useful for the optimal design and operation of the pyrolysis reactors. However, most of thermal degradation kinetics of plastics have been studied for commercial plastics. Therefore, in this work, the kinetics of thermal degradation of waste PP and HDPE obtained from a recycling center for waste plastics were studied using the thermogravimetric technique.

Thermogravimetric analysis (TGA) cannot be used to elucidate clear mechanism for the thermal degradation of a polymer. Nevertheless, the derivation of kinetic data in the study of polymer degradation using TGA has received increasing attention in the last decade [2-4], because it gives reliable information on the activation energy and the overall reaction order. Recently, many efforts have been devoted to developing new mathematical methods for kinetic analysis using TGA [5-7]. Deng and coworkers [8] developed a parallel competitive reaction model based on the assumption that the rate constant at any conversion is approximately equal to the rate constant of its neighboring conversion, which accounts for the type of bond scission and the state of scission of the polymeric chain at any time. Park and coworkers [9] proposed a kinetic analysis method using a dynamic model based on a modified power law, which accounts for the thermal degradation of a polymer at any time. The actual values of the kinetic parameters obtained using conventional thermogravimetric techniques are dependent not only on such factors as the atmosphere, sample mass, sample shape, flow rate, and heating rate but also upon the mathematical treatment used to evaluate the data [10]. In their studies of the kinetic analysis of thermo-
gravimetric data for the pyrolysis of styrene-butadiene rubber (SBR), Oh and coworkers [11] reported that tremendous variations occur depending upon the mathematical approach taken in the analysis. Therefore, in this study, to obtain kinetic parameters to describe the thermal degradation of waste PP and HDPE, the dynamic thermogravimetric analysis curve and its derivative were analyzed using a variety of analytical methods that have been previously reported in the literature [12-18].

Experimental

The kinetic analysis of the thermal degradation of waste PP and HDPE for nonisothermal conditions was investigated thermogravimetrically. The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50 at various heating rates between 10 and 30 °C/min. An electrically heated reaction tube was used (18-mm i.d.; 165-mm length). The sample was placed in a quartz cell of 6-mm diameter. The cell was then placed on a platinum crucible connected to a thermobalance. The carrier gas was supplied from a gas bottle and regulated using a gas flow meter. The variation of the sample mass with respect to the reaction temperature was detected by a photoelectric element and the weight-measuring circuits in the thermobalance. The signals were then transmitted to a personal computer through an analog-to-digital converter for subsequent data storage and plotting. To examine the thermal degradation, waste PP and HDPE and their blends were used in this study. The waste PP and HDPE samples were prepared by using an extruder after they had been selected by handsorting at a recycling center for waste plastics. The blend was mixed at 50% concentration by weight of waste PP. The initial mass of the sample was 13.9 ~ 14.3 mg. The experiments were performed under a nitrogen atmosphere at a flow rate of 50 mL/min and a purge time of 20 min.

Kinetic Models

All of the kinetic studies utilized the basic rate equation of conversion \( \alpha \) for thermal degradation under a nitrogen atmosphere:

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

(1)

where \( A, E, T, \) and \( R \) are the frequency factor (1/sec), the activation energy (J/mol), the reaction temperature (K), and the gas constant (8.314 J/mol \cdot K), respectively, and \( n \) denotes the overall reaction order.

Dynamic Method

In Equation (1), \( A \) is not strictly constant; it depends, based on collision theory [19], on \( \frac{1}{T} \). Therefore, if Equation (1) is used and a heating rate \( \beta = \frac{dT}{dt} \) (K/sec) is employed, it can be shown that

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

(2)

If the temperature rises at a constant heating rate \( \beta \), and the kinetic parameters at any weight-loss fraction is approximately equal to those of its neighboring conversion, then by differentiation of Equation (2),

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

(3)

Equations (2) and (3) give the following expressions for \( n \) and \( E \):

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

(4)

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

(5)

If the factor \( A_0 \) is determined, the values of \( n \) and \( E \) at any conversion can be obtained from Equations (4) and (5) by numerical methods. In a previous study [9], we derived Equation (6) from Equation (3) by setting \( d^2\alpha/dT^2 \) to zero at the maximum degradation rate.

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

(6)

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

Freeman–Carroll Method

This technique involves taking the basic equation (1) in the logarithmic form and utilizing the rates of weight loss at different temperatures [13]:

\[
\Delta \ln(\frac{d\alpha}{dt}) = n \Delta \ln(1-\alpha) - \frac{(E/RT) \Delta(1/T)}{2}
\]

(7)

In the case of the Freeman–Carroll method, to evaluate the constants in Equation (7), \( \Delta \ln(\frac{d\alpha}{dt}) \) is plotted against \( \Delta \ln(1-\alpha) \) for constant \( \Delta(1/T) \) values of 0.01. Although
Table 1. TG-DTG Data at Maximum Thermal Degradation Rate

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>Thermal degradation rate, $H_m$</th>
<th>Temperature, K</th>
<th>Conversion, $\alpha_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0513</td>
<td>0.0494</td>
<td>0.0430</td>
</tr>
<tr>
<td>20</td>
<td>0.0332</td>
<td>0.0334</td>
<td>0.0286</td>
</tr>
<tr>
<td>30</td>
<td>0.0299</td>
<td>0.0273</td>
<td>0.0241</td>
</tr>
</tbody>
</table>

this technique has been shown to be less subjective to changes in $n$, allowing $E$ values to be determined as a function of $\alpha$, the values generated were subject to large errors and did not compare favorably with the values generated using alternative techniques because discontinuities are frequently observed in the treatment of the experimental data. In this study, to remove the discontinuities in the treatment of data, from Equation (7) we obtain

$$\frac{\ln(\text{deg/dt})}{\Delta(1/T)} = -\frac{n\ln(1-\alpha)}{\Delta(1/T)} - \frac{E}{R}$$

(8)

To evaluate the constants in Equation (8), $\frac{\ln(\text{deg/dt})}{\Delta(1/T)}$ is plotted against $\frac{\ln(1-\alpha)}{\Delta(1/T)}$.

Flynn-Wall Method

This technique involves obtaining the temperatures at the maxima of the first-derivative weight-loss curves. If the basic equation (1) is used and a heating rate $\beta = dT/dt$ is employed, it can be shown that

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp(-E/RT)(1-\alpha)^n$$

(9)

Because the maximum rate occurs when $d^2\alpha/dT^2 = 0$, differentiation of Equation (9) with respect to $T$ and setting the resulting expression to zero gives

$$\frac{E}{RT_m^2(1-\alpha_m)^{n-1}} = \frac{A}{\beta} \exp(-E/RT_m)$$

(10)

where $T_m$, $H_m$, and $\alpha_m$ are the peak temperature, the peak height of the DTG curve, and the degree of conversion at the peak temperature, respectively. Substituting Equation (10) into Equation (9) yields the following expression for the overall reaction order:

$$n = \frac{E(1-\alpha_m)}{RT_m^2H_m}$$

(11)

The activation energy can also be calculated from two peak temperatures at different heating rates as follows:

$$E = R \left(\frac{T_{m2}T_{m1}}{T_{m1}-T_{m2}}\right) \ln\left(\frac{\beta_2}{\beta_1}\right) \left(\frac{1-\alpha_{m1}}{1-\alpha_{m2}}\right)^{n-1} \left(\frac{T_{m2}}{T_{m1}}\right)^2$$

$$\approx R \left(\frac{T_{m2}T_{m1}}{T_{m1}-T_{m2}}\right) \ln\left(\frac{\beta_2}{\beta_1}\right) \left(\frac{T_{m2}}{T_{m1}}\right)^2$$

(12)

where the subscripts 1 and 2 refer to the two different heating rates. The equation above is conceptually equal to the differential method proposed by Flynn and Wall [18], who indicated that $\alpha_m$ was unlikely to vary with respect to the heating rate. Table 1 shows the TG and DTG data obtained at the maximum thermal degradation rate used for this technique.

Kissinger Method

Kissinger [12] assumed that $n(1-\alpha_m)^{n-1}$ was independent of $\beta$ and very nearly equal to unity for a first-order reaction. Thus, the following expression, which can be derived from Equation (10),

$$\frac{d\ln(\beta/T_m^n)}{d(1/T_m)} = -\frac{E}{R}$$

(13)

allows the activation energy to be determined from a plot of $\ln(\beta/T_m^n)$ against $1/T_m$.

Friedman Method

This technique is based on the intercomparison of the rates of weight loss $d\alpha/dt$ for a given conversion $\alpha$ determined using different heating rates $\beta$ [15]. After taking the logarithm of Equation (1), we obtain

$$\ln(d\alpha/dt) = \ln(A(1-\alpha)^n) - E/RT$$

(14)

Using this equation it is possible to obtain values for $E$, over a wide range of conversions, from the slope $-E/R$ by plotting $\ln(d\alpha/dt)$ against $1/T$. For fixed $\alpha$, the first term on the right-hand side of Equation (14) is constant. Thus, the apparent activation energy can be obtained from the average value of the activation energy for different values of $\alpha$. From the first term on the right-hand side of Equation (14), we obtain

$$\ln(A(1-\alpha)^n) = \ln A + n\ln(1-\alpha)$$

(15)

The next step is to obtain the values of $\ln(A(1-\alpha)^n)$ at
various heating rates at a given $\alpha$ and plot these values against $\ln(1-\alpha)$ to yield a straight line having slope $n$.

**Coats-Redfern Method**

From Equation (9), it can be shown that

$$\frac{\frac{d\alpha}{(1-\alpha)^n}}{=\frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT}$$

which, on integrating, provides the following expression:

$$F(\alpha) = \int_{0}^{\alpha} \frac{ \frac{d\alpha}{(1-\alpha)^n} }{=\frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT}$$

The integral approximation used with this technique is to consider Equation (17) when it can be shown that

$$\int_{0}^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{1-(1-\alpha)^{1-n}}{1-n} \quad \text{for} \quad n\neq 1$$

$$= -\ln(1-\alpha) \quad \text{for} \quad n=1$$

while

$$\frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT = \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right)$$

(19)

After taking logarithms, the following equations can be obtained:

$$\ln\left(\frac{1-(1-\alpha)^{1-n}}{T(1-n)}\right) = \ln\left(\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) + \frac{E}{RT}\right)$$

for $n\neq 1$

(20)

and

$$\ln\left(\frac{-\ln(1-\alpha)}{T^n}\right) = \ln\left(\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) + \frac{E}{RT}\right)$$

for $n=1$

(21)

Thus, plots of

$$\ln\left(\frac{1-(1-\alpha)^{1-n}}{T(1-n)}\right) \quad \text{vs.} \quad \frac{1}{T} \quad \text{for} \quad n\neq 1$$

(22)

$$\ln\left(\frac{-\ln(1-\alpha)}{T^n}\right) \quad \text{vs.} \quad \frac{1}{T} \quad \text{for} \quad n=1$$

(23)

results in straight lines whose slopes equal $-E/R$ for correctly chosen values of $n$ [16].

**Horowitz-Metzger Method**

For a first-order reaction, the following equation can be obtained from Equation (17):

$$-\ln(1-\alpha) = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT$$

(24)

Using a series of approximations and simplifications to integrate the right-hand side of Equation (24), the following equations can be obtained:

$$-\ln(1-\alpha) = \exp\left(-\frac{E}{RT}\right)$$

(25)

and, eventually,

$$\ln\left(\frac{1}{(1-\alpha)}\right) = \frac{E}{RT}$$

(26)

where $T_i$ is the temperature at which 1- $\alpha$ = 1/exp = 0.368 and $\theta = T - T_i$. Thus a plot of $\ln\left(\frac{1}{1-\alpha}\right)$ against $\theta$ allows the activation energy to be determined [14].

**Ozawa Method**

This method represents a relatively simple approach to determining activation energies directly from weight loss and temperature data obtained at several heating rates. In essence, this technique assumes that $A$, (1- $\alpha$)$^n$, and $E$ are independent of $T$, while $A$ and $E$ are independent of $\alpha$, wherein the variables given in Equation (17) may be separated and integrated to give, in logarithm form,

$$\log F(\alpha) = \log(AE/R) - \log\beta + \log\left(\frac{E}{RT}\right)$$

(27)

Using Doyle's [17] approximation for the integral, which allows $E/RT > 20$, Equation (27) may be expressed as

$$\log F(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta - 2.315 - 0.4567 \frac{E}{RT}$$

(28)

The activation energy $E$ can, therefore, be obtained from a plot of $\log\beta$ against $1/T$ for a fixed degree of conversion because the slope of such a line is given by $-0.4567E/R$.

**Results and Discussion**

Figure 1 shows the TG curves of waste PP, HDPE, and their blends recorded under a nitrogen atmosphere at various heating rates. We found that the curves were displaced to higher temperatures because of a heat transfer lag at increased heating rates. For all samples, residues of less than 0.3 mg were obtained, based on a sample weight of 13.9 ~ 14.3 mg. Therefore, we conclude that nearly all of the material subjected to degradation was transformed into volatile material. The typical TG and DTG curves of waste PP, HDPE, and their blends recorded under a nitrogen atmosphere at a heating rate of 30 °C/min are presented in Figure 2. The TG
curves in Figure 2 show that the blend of waste PP and HDPE results in thermal degradation occurring with a gentler slope. It was also found that the thermal degradation of waste PP took place most rapidly. From the DTG curves of Figure 2, it was found that DTG curves are not smooth. We have observed similar phenomena previously [9,11]. Thus, we believe that the thermogravimetric phenomena are accompanied by electric noise. We observed just one peak for the blends even though the waste PP and HDPE were mixed.

Figure 3 shows the plots of $1/T_m$ against $\ln \beta$ used to calculate the factor $A_0$ in Equation (6). These plots are straight lines having slopes equal to $-E_m/RT$; thus, the activation energy ($E_m$) at the maximum degradation rate can be obtained easily. The values of $A_0$ obtained by substituting this value of $E_m$ back into the intercept of the $y$ axis are summarized in Table 2. The activation energies and the overall reaction orders upon conversion obtained from $A_0$ and Equations (4) and (5), and the TG data obtained by numerical methods are shown in Figures 4 and 5. From Figure 4, the Dynamic method gave activation energies of 217.0 ~ 233.2, 269.2 ~ 292.4, and 152.3 ~ 174.9 kJ/mol for waste PP, HDPE, and their blends, respectively. Cooney and coworkers [10] concluded that the use of a multiple heating rate method represented more realistically the variety of heating rates used for the thermal degradation of polymers because of the wide
Table 2. Determination of Factor $A_0$ in Equation (2)

<table>
<thead>
<tr>
<th>Heating rate $\beta$ (K/min)</th>
<th>Activation energy, $E_m$ (kJ/mol)</th>
<th>Factor, $A_0$ (s$^{-1}$K$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. Activation energy upon conversion according to the Dynamic method.

Figure 5. Overall reaction order upon conversion according to the Dynamic method.

variations obtained when using various heating rates in a single-heating-rate technique. However, although the Dynamic method used the single-heating-rate experiments, the results were only slightly affected by the heating rates. Figure 5 shows the overall reaction order upon conversion; it too is only slightly affected by the heating rates. Figure 6 shows the activation energy upon conversion, according to the Friedman method; activation energies of 185.0$\sim$241.7, 205.6$\sim$290.9, and 120.0$\sim$237.0 kJ/mol were obtained for waste PP, HDPE, and their blends. The activation energies upon conversion, obtained from the Ozawa method, are shown in Figure 7; the activation energies were 193.0$\sim$245.1, 251.5$\sim$280.2, and 98.2$\sim$165.0 kJ/mol for waste PP, HDPE, and their blends, respectively.

For comparative purposes the results from the analytical methods used in this study are summarized in Table 3; the kinetic parameters obtained from the Dynamic, Friedman, and Ozawa methods are the average values calculated from Figures 4$\sim$7. We can see that there are tremendous variations in the calculated kinetic parameters depending on the mathematical approach used for
Figure 6. Activation energy upon conversion according to the Friedman method.

Figure 7. Activation energy upon conversion according to the Ozawa method.

Table 3. Kinetic Parameters Obtained using a Variety of Analytical Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction order, ( n )</th>
<th>Activation energy, ( E ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic Method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 10 °C/min</td>
<td>1.25(^a)</td>
<td>1.25(^a)</td>
</tr>
<tr>
<td>at 20 °C/min</td>
<td>1.29(^a)</td>
<td>1.26(^b)</td>
</tr>
<tr>
<td>at 30 °C/min</td>
<td>1.12(^a)</td>
<td>1.09(^b)</td>
</tr>
<tr>
<td>Freeman-Carroll</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 10 °C/min</td>
<td>1.19</td>
<td>1.21</td>
</tr>
<tr>
<td>at 20 °C/min</td>
<td>0.52</td>
<td>0.92</td>
</tr>
<tr>
<td>at 30 °C/min</td>
<td>0.95</td>
<td>0.92</td>
</tr>
<tr>
<td>Flynn-Wall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 10 °C/min</td>
<td>0.30</td>
<td>0.35</td>
</tr>
<tr>
<td>at 20 °C/min</td>
<td>0.43</td>
<td>0.55</td>
</tr>
<tr>
<td>at 30 °C/min</td>
<td>0.48</td>
<td>0.68</td>
</tr>
<tr>
<td>Kissinger</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00(^b)</td>
<td>1.00(^b)</td>
</tr>
<tr>
<td>Friedman</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.64</td>
<td>0.43</td>
</tr>
<tr>
<td>Integral method</td>
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<tr>
<td>Horowitz-Metzger</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 10 °C/min</td>
<td>1.00(^b)</td>
<td>1.00(^b)</td>
</tr>
<tr>
<td>at 20 °C/min</td>
<td>1.00(^b)</td>
<td>1.00(^b)</td>
</tr>
<tr>
<td>at 30 °C/min</td>
<td>1.00(^b)</td>
<td>1.00(^b)</td>
</tr>
<tr>
<td>Coats-Redfern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 10 °C/min</td>
<td>0.50(^a)</td>
<td>0.00(^b)</td>
</tr>
<tr>
<td>at 20 °C/min</td>
<td>0.50(^b)</td>
<td>0.00(^b)</td>
</tr>
<tr>
<td>at 30 °C/min</td>
<td>0.50(^b)</td>
<td>0.00(^b)</td>
</tr>
<tr>
<td>Ozawa</td>
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</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Average value
\(^b\) Assumed value
\(^c\) Best-fit value
the kinetic analyses. These observations clearly indicate the problems in selecting and utilizing the different analytical methods to describe the thermal degradation of waste PP and HDPE. In the differential methods, the Freeman-Carroll method gave varying results at various heating rates, but the kinetic parameters from the Flynn-Wall method were only slightly affected by the heating rate. However, the Flynn-Wall method uses only one point, i.e., the point of the maximum degradation rate, and is, therefore, regarded in some respects, as having only limited applicability. Although Kissinger method uses multiple heating rate experiments, it also uses only the point of maximum degradation rate as well as the assumption of a first-order reaction for the thermal degradation of the polymer. The Dynamic and Friedman methods can give the activation energies upon conversion of waste PP and HDPE at any time. In particular, although the Dynamic method used multiple heating rate experiments to determine the factor $A_0$, the activation energies for each heating rate could be obtained and the results were affected only slightly by the heating rates. In addition, the Dynamic method gave the overall reaction upon conversion at any time, whereas the Friedman method could not give the overall reaction for the thermal degradation of waste PP and HDPE at any time. For the integral methods, the Horowitz-Metzger method uses the assumption of a first-order reaction for thermal degradation of the polymer, but the results were only slightly affected by the heating rate. The Coats-Redfern method was applied to our data and the best-fit values for each heating rate were determined by employing values of the reaction order ($n$) of 0, 0.5, 1.0, 1.5, and 2.0. The best values of overall fit were obtained using $n = 0.5$, with the exception of waste HDPE, for which the best fit of the data was obtained using $n = 0$. However, this approach gave activation energies that varied with respect to the heating rate. The Ozawa method not only gives the activation energies upon conversion of waste PP and HDPE at any time but also it uses multiple heating rate experiments. However, the Ozawa method is only applicable to the calculation of the activation energy. In conclusion, we believe that the best methods for the kinetic analysis of the thermal degradation of waste PP and HDPE are the Dynamic and Friedman methods. We also found that the activation energy of the waste blend was smaller than those of waste PP and HDPE.

Finally, in a comparison of the kinetic parameters of the thermal degradation of commercial and waste PP and HDPE samples, the kinetic parameters reported in the literatures are summarized in Table 4. We observe that the activation energies for waste PP and HDPE are slightly smaller than those of commercial PP and HDPE samples.

### Conclusions

From this study, we found that there are tremendous variations in the calculated kinetic parameters depending upon the mathematical approach taken for the analysis. The Freeman-Carroll and Coats-Redfern methods gave kinetic results that varied with respect to the heating rate. The Flynn-Wall and Kissinger methods use only the point of maximum degradation rate, and they are, therefore, regarded in some respects as having only limited applicability. In addition, the Kissinger and Horowitz-Metzger methods use the assumption of a first-order reaction for the thermal degradation of polymers, and the Ozawa method is only applicable to calculation of the activation energy. Therefore, we believe that the best methods for the kinetic analysis of the thermal degradation of waste PP and HDPE are the Dynamic and Friedman methods. We also found that the activation energy of the waste blend was smaller than those of the waste PP and HDPE samples. From a comparison of the kinetic parameters of both commercial and waste PP and
HDPE samples, we found that the activation energies of 

References

1. Y. Uemura, M. Azeura, Y. Ohzuno, and Y. Hatate, 
   32, 4353 (1986).
3. A. Jimenez, V. Berenguer, J. Lopez, and A. Sanchez, 
   Kim, W. Y. Lee, S. H. Song, S. B. Lee, and M. J. 
6. R. W. J. Westerhout, J. Waanders, J. A. M. Kuipers, 
   and W. P. M. van Swaaij, Ind. Eng. Chem. Res., 36, 
7. K. S. Chen, R. Z. Yeh, and Y. R. Chang, 
13. E. S. Freeman and B. Carroll, J. Phys. Chem., 62, 
    394 (1958)
    1464 (1963).
    (1964).
    (1964).
    Standards-A. Physics and Chemistry, 70A, 487 
    (1966).
19. S. R. Turn, An Introduction to Combustion: 
21. K. Murata and T. Makino, Nippon Kagaku Kaishi, 2, 
    192 (1975).
23. C.-H. Wu, C.-Y. Chang, J.-L. Hor, S.-M. Shih, 
24. R. W. J. Westerhout, J. Waanders, J. A. M. Kuipers, 
    and W. P. M. van Swaaij, Ind. Eng. Chem. Res., 36, 