A Kinetic Analysis of the Thermal Degradation of Pyrolytic Heavy Oils obtained from Kiln Pyrolysis Process

Kyong Hwan Lee · Woo-Teck Kwon* · Sea Cheon Oh**

Department of Energy Conversion Technology, Korea Institute of Energy Research, Daegon Korea
Department of Ceramics Building Materials*, Korea Institute of Ceramic Engineering and Technology, Seoul, Korea
Department of Environmental Engineering**, Kongju National University†, 275, Budae-dong, Cheonan, Chungnam, 330-717, Korea
(Received April 12, 2011, Revised May 30, 2011, Accepted June 2)

Abstract

The kinetic analysis of the thermal degradation of pyrolytic heavy oils obtained from mixed waste plastics by kiln pyrolysis process has been studied by conventional thermogravimetric technique with various heating rates in nitrogen atmosphere. Results of kinetic analysis show that the activation energies are 24.4–26.5 kJ/mol and the reaction orders are 1.0–1.25, respectively. To verify the effectiveness of the kinetic analysis method used in this work, the experimental values were compared with those of the numerical integration results using kinetic parameters obtained in this work. It was found that the kinetic analysis method used in this work gave the reliable kinetic parameters of the thermal degradation of pyrolytic heavy oils.

Key words: kinetic analysis, thermal degradation, pyrolytic heavy oil, kiln pyrolysis process

† Corresponding author
E-mail: ohsec@kongju.ac.kr
Tel : 041-521-9423
1. Introduction

As quantitites of municipal and industrial organic wastes increase, the thermal treatment of solid wastes by pyrolysis or incineration has received considerable attention. A proper thermal treatment system not only resolves the disposal problem but also recovers energy from wastes. In the last years, many efforts have been devoted to the development of pyrolysis process for waste plastics[1–3]. Recently, pyrolysis reactor of kiln type has been studied to recover fuel oil from mixed waste plastics [4]. Rotary kilns have been evaluated for a variety of organic wastes such as wood, used tyres, plastic wastes, etc.[5]. Therefore, pyrolysis process using rotary kiln has been recognized as an effective method to recover fuel oil from mixed waste plastics including plastics, rubber, glass, sand and dirt of all kinds. However, pyrolytic heavy oils containing high molecular components are formed where mixed waste plastics are thermally cracked, and are not good to use as alternative industrial liquid fuel oil. Therefore, the retreatment of pyrolytic heavy oil is required by thermal or catalytic cracking. It is well known that the kinetic investigation is very important to get information for rationally designing the reactor for the thermal degradation. The thermal degradation kinetics in polymeric materials is generally quite complicated due to the nature of polydispersity of polymer chains[6]. Thermogravimetric analysis (TGA) cannot be used to elucidate a clear mechanism of thermal degradation. Nevertheless, much effort has been recently devoted to developing a new mathematical method for kinetic analysis using TGA because it gives reliable information of the pre-exponential factor, the activation energy, and the overall reaction order[7–9]. In this work, the kinetic analysis method using the integral method based on Arrhenius form was used to obtain the kinetic parameters such as the apparent activation energy, the overall reaction and the pre-exponential factor. And this method was applied to the kinetic analysis of thermal degradation of pyrolytic heavy oils obtained from mixed waste plastics by kiln pyrolysis process. To verify the effectiveness of the kinetic analysis method used in this work, the experimental values were compared with those of the numerical integration results using kinetic parameters obtained in this work. Also the kinetic results obtained from the kinetic analysis method proposed in this work were compared with those of the kinetic results using the various analytical methods in the literature[10].

2. Kinetic Analysis

When the polymeric materials are subject to heating condition, complicated process occurs, such as random chain scission, end-chain scission, chain stripping, cross-linking and coke formation. In this work, there is no intention to describe fundamental chemical mechanisms of the thermal degradation. This work focuses on the measurement of apparent kinetic parameters useful for chemical engineering design. In the kinetics of thermal degradation of polymeric materials using TGA, it is usual to assume that the degradation rate, \( \frac{da}{dt} \) is proportional to the concentration of materials which has to react. Therefore, by power law model it can be expressed as

\[ \frac{da}{dt} = k(a_{0} - a)^n \]

where \( a_{0} \) is the initial concentration of the material, and \( n \) is the order of the reaction. The rate constant \( k \) is related to the activation energy and the pre-exponential factor through the Arrhenius equation:

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

where \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. The rate constant \( k \) is a function of temperature and can be obtained by differentiating the equation above with respect to temperature.

\[ \frac{da}{dt} = k(a_{0} - a)^n = \frac{d}{dt} \left( A \exp \left( -\frac{E_a}{RT} \right) (a_{0} - a)^n \right) \]

By integrating this equation over the range of concentration, the integral method can be used to obtain the kinetic parameters.
\[
\frac{da}{dt} = K(1-a)^n
\]  
(1)

where \( K \) and \( n \) are the rate constant \( (1/min) \), the reaction order and the weight loss fraction, respectively. The temperature dependence on the rate constant \( K \) may be described by the Arrhenius expression as follows:

\[
K = A \exp(-E/RT)
\]  
(2)

Combining Equations (1) and (2), the overall degradation rate is given by Equation (3).

\[
\frac{da}{dt} = A(1-a)^n \exp(-E/RT)
\]  
(3)

where \( A \), \( E \), \( T \) and \( R \) are the pre-exponential factor \( (1/min) \), the activation energy \( (J/mol) \), the temperature of reaction \( (K) \) and the gas constant \( (8.314 J/mol K) \), respectively. However, the pre-exponential factor, \( A \) is not strictly constant but depends on the reaction temperature \([11]\). And if the heating rate \( \beta = dT/dt \) \((K/min)\) is employed, it can be shown that

\[
\frac{da}{dT} = \frac{A_0}{\beta} T^\alpha (1-a)^n \exp(-E/RT)
\]  
(4)

where \( m \) is the order on the degradation temperature. From Equation (4), it can be shown that

\[
\frac{1}{(1-a)^n} \frac{da}{(1-a)^n} = \frac{A_0}{\beta} T^\alpha \exp(-E/RT)dT
\]  
(5)

where, on integrating, provides the following expression:

\[
\int_0^1 \frac{da}{(1-a)^n} = \frac{A_0}{\beta} \int_0^T T^\alpha \exp(-E/RT)dT
\]  
(6)

The integral approximation is to consider Equation (6) when it can be shown that

\[
\frac{A_0}{\beta} \int_0^T T^\alpha \exp(-E/RT)dT =
\]

\[
\frac{A_0 R}{\beta E} T^{m+2} \left(1-(m+2) \frac{RT}{E}\right) \exp(-E/RT)
\]  
(7)

while

\[
\int_0^1 \frac{da}{(1-a)^n} = \frac{1-(1-a)^n}{1-n} \quad \text{for } n \neq 1
\]  
(8)

\[
= -\ln(1-a) \quad \text{for } n = 1
\]  
(9)

After taking logarithms, the following equations can be obtained:

\[
\ln \left( \frac{1-(1-a)^n}{1-n} \right) = F - \frac{E}{RT} \quad \text{for } n \neq 1
\]  
(10)

\[
\ln(-\ln(1-a)) = F - \frac{E}{RT} \quad \text{for } n = 1
\]  
(11)

where

\[
F = \ln \left[ \frac{A_0 R}{\beta E} T^{m+2} \left(1-(m+2) \frac{RT}{E}\right) \right]
\]  
(12)

Thus, plots of

\[
\ln \left( \frac{1-(1-a)^n}{1-n} \right) \text{ vs. } \frac{1}{T} \quad \text{for } n \neq 1
\]  
(13)

\[
\ln(-\ln(1-a)) \text{ vs. } \frac{1}{T} \quad \text{for } n = 1
\]  
(14)

result in straight lines whose slopes equal \(-E/RT\) for correctly chosen values of \( n \).

Also, \( A_0 \) and \( m \) can be calculated from the activation energy \( E \) and the intercept \( F \) on the \( Y \) axis by using least square method.

### 3. Results and Discussion

The samples of pyrolytic heavy oils used in kinetic analysis of this work were obtained from mixed waste plastics by field pyrolysis process using rotary kiln. Proximate analysis of the sample used in this work is shown in Table 1. From Table 1, it can be seen that the volatile material is major component and the
amount is 99.3 wt%. And there are no fixed carbon and ash. This is due to the factor that samples used in this work are obtained from mixed waste plastics by pyrolysis process.

**Table 1. Proximate analysis of pyrolytic heavy oils used in this work**

<table>
<thead>
<tr>
<th>Item</th>
<th>Weight fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moisture</td>
<td>0.70</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>99.3</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>0.00</td>
</tr>
<tr>
<td>Ash</td>
<td>0.00</td>
</tr>
</tbody>
</table>

For kinetic analysis, the thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. The experiments were carried out in a nitrogen atmosphere with a flow rate of 50ml/min and a purge time of 20min.

**Fig. 1. TG curves of samples in nitrogen atmosphere at various heating rates.**

The samples were studied at various heating rates between 10 and 50°C/min. The initial masses of the sample were 12.23–15.50mg. Fig. 1 shows the variations of the TG curves with respect to temperature for various heating rates in pure nitrogen. Obviously, there are one principal reaction stages. It was also seen from Fig. 1 that the weight loss curves of pyrolytic heavy oils were displaced to higher temperatures due to the heat transfer lag with increased heating rate. And distinct mass changes over the temperature of 50–400°C were investigated. A rapid increases in the conversion were seen above 100°C. And when the degradation temperature attained 400°C, about 99% of conversion was obtained.

Figs. 2–6 show the application of kinetic analysis method used in this work at heating rates of 10, 20, 30, 40 and 50°C/min, respectively. This method has been applied to our data and the best fit values for each heating rate were determined by employing reaction order values \( n \) of 0.0–2.0 with interval of 0.25.

**Fig. 2. Application of the kinetic analysis method at heating rate of 10°C/min.**

The best overall fit values were obtained using a value for \( n=1.25 \) in the cases of heating rates of 10, 20 and 30°C/min with
The kinetic parameters calculated by this method with these values of $n$ were summarized in Table 2. From Table 2, the kinetic method used in this work gave the apparent activation energies of 24.4–26.9 kJ/mol and the order on the degradation temperature of 2.26–2.15, respectively. Also from this work it was obtained that factor $A_0$ were $5.0123 \times 10^2$–$2.7612 \times 10^4$.

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 mathematical treatment used to evaluate the data. Therefore, it is necessary to compare the kinetic results with those of various analytical methods.

Table 2. The kinetic parameters obtained from this work

<table>
<thead>
<tr>
<th>Method</th>
<th>β (°C/min)</th>
<th>n</th>
<th>E (kJ/mol)</th>
<th>A0 (min⁻¹)</th>
<th>k ¹/²</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeman–Carroll</td>
<td>10</td>
<td>1.83</td>
<td>5.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.39</td>
<td>10.7</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.06</td>
<td>3.0</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>6.2</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chatterjee–Conrad</td>
<td>10</td>
<td>1.00</td>
<td>16.0</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.00</td>
<td>15.6</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.00</td>
<td>17.6</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>9.3</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flynn-Wall</td>
<td>10</td>
<td>1.00</td>
<td>21.4</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.00</td>
<td>28.7</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.00</td>
<td>51.6</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>47.4</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kissinger</td>
<td>10–50</td>
<td>1.00</td>
<td>32.5</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Friedman</td>
<td>10–50</td>
<td>1.00</td>
<td>51.1</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozawa</td>
<td>10–50</td>
<td>1.00</td>
<td>55.8</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 shows the kinetic parameters calculated by various analytical methods proposed in the literature [10]. From Table 3, it was seen that the kinetic parameters were varied with respect to analytical methods. Above all, the kinetic parameters were also varied with heating rates. These observations clearly indicate the problems to describe the thermal degradation of pyrolytic heavy oils. However, the kinetic parameters obtained from this work were little affected by heating rates with exception of factor A0.

Figure 7 also shows the TG data and the computed values by the kinetic parameters obtained from this work and the numerical integration of Equation (5) to verify the performance of the kinetic analysis method used in this work. It was seen that the computed values agreed very well with the TG data, and the kinetic analysis method used in this work gave a reliable value of kinetic parameters for the thermal degradation of pyrolytic heavy oils obtained from mixed waste plastics by kiln pyrolysis process.

Table 3. The kinetic parameters obtained from various analytical methods proposed in the literature [10]

<table>
<thead>
<tr>
<th>Method</th>
<th>β (°C/min)</th>
<th>n</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeman–Carroll</td>
<td>10</td>
<td>1.83</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.39</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.06</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>6.2</td>
</tr>
<tr>
<td>Chatterjee–Conrad</td>
<td>10</td>
<td>1.00</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.00</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.00</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>9.3</td>
</tr>
<tr>
<td>Flynn-Wall</td>
<td>10</td>
<td>1.00</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.00</td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.00</td>
<td>51.6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.00</td>
<td>47.4</td>
</tr>
<tr>
<td>Kissinger</td>
<td>10–50</td>
<td>1.00</td>
<td>32.5</td>
</tr>
<tr>
<td>Friedman</td>
<td>10–50</td>
<td>1.00</td>
<td>51.1</td>
</tr>
<tr>
<td>Ozawa</td>
<td>10–50</td>
<td>1.00</td>
<td>55.8</td>
</tr>
</tbody>
</table>

4. Conclusion

The kinetic analysis of the thermal degradation of pyrolytic heavy oil obtained from mixed waste plastics by kiln pyrolysis process has been studied. Distinct mass changes over the temperature of 50–400 °C were investigated and the rapid increases in the conversion were seen over 100 °C. From this work, it was also found that the overall reaction orders were 1.0–1.25, whereas the apparent activation energies were 24.4–26.9...
kj/mol. From the comparison of kinetic results with various analytical methods, it was found that the kinetic parameters were varied with respect to heating rates. These observations clearly indicate the problems to describe the thermal degradation of pyrolytic heavy oils. However, the kinetic parameters obtained from this work were little affected by heating rates. Also from the comparison of the TG data and the computed values by the kinetic parameters obtained from this work, it was seen that the computed values agreed very well with the TG data, and the kinetic analysis method used in this work gave a reliable value of kinetic parameters for the thermal degradation of pyrolytic heavy oils.

References


