Resources Recovery of Waste Rayon by Pyrolysis: Kinetics Study

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Abstract—Rayon derived from natural biomass fibers are extensively used in the production of a wide range of commercial, industrial, and engineering products, especially rayon clothes. The rayon discharged by textile industry, and consumers are becoming a large proportion of wastes. The conversion of rayon to various useful materials such as lower molecular weight organic compounds (liquid fuels and combustible gas) and carbonaceous fibers or activated carbons via pyrolysis not only solves the disposal problem but also matches the wastes minimization and resource utilization. Before considering the thermal treatment of utilization of rayon clothes, one should investigate the behavior of rayon alone during the thermal treatment. The pyrolysis of rayon is thus examined with a thermal gravimetric analyzer (TGA). The kinetics of the thermal pyrolysis of rayon is conducted using nitrogen as the carrier gas in 378-800K and at various constant heating rates ($\beta$) of 5, 12, and 20K/min. The results indicate that the entire pyrolysis process of rayon under the experimental conditions of this investigation can be described by two competitive reactions forming volatiles and residues (including carbon). The corresponding activation energies ($E$), reaction orders ($n$) and frequency factors ($A$) of volatiles and char formed by the two competitive (parallel) reactions of pyrolysis of rayon are 171.6 and 191.8 kJ/mol of $E$, 1 and 1.5 of $n$, and $4.3 \times 10^{11}$ and $5.6 \times 10^{12}$ s$^{-1}$ of $A$, respectively. All this information is useful to the proper design of a pyrolysis system of rayon.

Key Words: Rayon, Pyrolysis, Resources recovery, Kinetics, Char formation

INTRODUCTION

Rayon derived from natural biomass fibers are extensively used in the production of a wide range of commercial, industrial, and engineering products. The waste rayon from textile industry and consumers are becoming a large proportion of wastes. There is an attracting interest in developing resources utilization process to produce useful products from biomass waste of rayon, which can off-set the costs of waste disposal.

The pyrolysis kinetics of cellulosic materials has been investigated by several investigators. The thermal pyrolysis reaction of cellulosic materials is mainly first order with the activation energy in the range of 150-250 kJ/mol (Conesa et al., 1995; Devallencourt et al., 1996; Huang and Li., 1998; Yuan-wen and Dillimore., 1998). Also, Liu et al. (2003) investigated the thermal pyrolysis behaviors of two types of rayon fibers derived from wood pulp and
and cotton pulp in the temperatures range of 200-500°C by thermal gravimetry (TG) and differential TG (DTG) in an argon atmosphere. Results obtained by the iteration method indicated that both types of rayon fibers have the same reaction order \( n \) (0.9) and similar kinetic behaviors, comparable with those of other cellulosic materials. Determined by the modified Friedman equation, the values of activation energy \( E \) and frequency factor \( A \) of wood-derived and cotton-derived rayon fibers are 231.57 and 231.26 kJ/mol, and 2.66 × 10^{21} \text{ and } 1.78 × 10^{21} \text{ min}^{-1}, respectively (Liu et al., 2003).

The production of activated carbon from waste rayon is one of the major areas under investigation (Pastor et al., 1999; Rodriguez-Reinoso et al., 2000a, 2000b; Huidobro et al., 2001). The pre-formed activated carbon derived from the pyrolysis of biomass natural fiber textile waste was studied (Williams and Reed, 2003). Viscose rayon cloth was carbonized under a wide range of experimental conditions, including carbonization procedures (Pastor et al., 1999), carbonization on CO\(_2\) activation (Rodriguez-Reinoso et al., 2000b), isothermal stage near the decomposition temperature (Rodriguez-Reinoso et al., 2000a), decomposition in air atmosphere (Liu et al., 2002), physical activation (Rodriguez-Reinoso et al., 2000a), and chemical activation (Huidobro et al., 2001). Impregnation of viscose rayon fabric with different chemicals modified the pyrolysis process. Highest increase in yield corresponded to AlCl\(_3\) and H\(_2\)PO\(_4\). H\(_2\)PO\(_4\) developed the widest microporosity, while Na\(_2\)HPO\(_4\) produced a large development of mesoporosity (Huidobro et al., 2001). Also, Kumar et al. (1997) pointed out that the pyrolysis of phosphoric acid pretreated viscose rayon cloth under a carbon dioxide atmosphere leads to widening of pores above 850°C. Referred to the kinetic study of decomposition of viscose rayon in the presence of inorganic additives, Venkateswaran et al. (1990) studied the effect due to the addition of ammonium chloride, calcium chloride, and a mixture of calcium chloride and ammonium chloride through thermogravimetry. The changes in the values of activation energy, order of reaction, and char yield were also examined. For the adsorption effects of polar methyl-ethyl-ketone (MEK) and non-polar benzene vapors on viscose rayon-based activated carbon fiber (ACF), Huang et al. (2002) studied the gas adsorption on the samples by the gravimetric method and fitted the adsorption isotherms by Dubinin-Radushkevich (DR) equation. However, the experimental results indicated that ACF with different pore texture and surface composition exhibited different adsorption and desorption behaviors for polar and non-polar vapors. Other researches on the utilization of rayon included: (1) synthesis of silicon carbide whiskers (SiC (w)) by the pyrolysis of rayon fibers impregnated with sol-gel-derived SiO\(_2\) (Vasantha et al., 2000) and (2) oxidative chemical polymerization of aniline by using peroxysulphate and peroxomonsulphate as initiators in an acidic medium in the presence of rayon fiber (Anbarasan et al., 2001).

The above studies provided some useful information of resources utilization and kinetics of pyrolysis and thermal treatment of rayon, however, gave no data about the detailed kinetic model of pyrolysis of rayon. It is thus the aim of the present work to study the thermal pyrolysis of rayon with the viewpoint of providing a kinetic model considering the pyrolysis of rayon, and formation of volatiles and carbon residue fraction from the pyrolysis of rayon. The pyrolysis is performed by the use of a dynamic thermogravimetric (TG) reaction system at various temperature-programmed constant heating rates (\( \beta \)) of 5, 12, and 20K/min in nitrogen atmosphere. The corresponding activation energies (\( E \)), frequency factors (\( A \)) and reaction orders (\( n \)) of reactions (formation of volatiles and carbon) are determined.

**EXPERIMENTAL**

**Materials**

The material sample used in this study is commercial-grade rayon. Nitrogen gas for the purge gas, with 99.99% purity, is purchased from the Ching-Feng-Haeng Co. Ltd. in Taipei, Taiwan. The obtained rayon is first cut for 0.5 × 0.5 cm square size and dried in a recycle ventilation drier for 2 h at 378K before use. The moisture, ash, and combustible of rayon are 11.36, 0.13, and 88.51%, respectively. The elemental analysis of the rayon sample is listed in Table 1. From Table 1, the molecular formula of the rayon sample is CH\(_{1.09}\)O\(_{0.93}\) with the H/C mole ratio of 1.99.

**Thermogravimetry**

The thermogravimetric system (Shimadzu TGA-51) used for the kinetic studies, which is the same as that employed in the previous study (Shie et al., 2002b), is schematically shown in Fig. 1. It mainly consists of electrobalance and furnace units. Some specifications of balance mechanism are: balance type of taut band, capacity of 10 g, resolution of 1 µg and accuracy of 1% of each measuring range. The furnace unit has an electrically heated reaction tube of 20 mm in inner diameter and 170 mm in length. A sample (5 ± 0.5 mg) is placed in a Pt cell of 6 mm in diameter and 2.5 mm in depth. The cell is then put on a Pt sample pan that is hung by a quartz suspension wire (155 mm long) and connected to the balance mechanism. The temperatures of furnace reaction tube
Table 1. Elemental analyses of rayon and solid residues at different temperatures. Heating rate ($\beta$) = 5K/min.

<table>
<thead>
<tr>
<th>Dry Rayon</th>
<th>700K</th>
<th>800K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>C</td>
<td>41.49 (0.11)</td>
<td>73.11 (1.04)</td>
</tr>
<tr>
<td>H</td>
<td>6.89 (0.05)</td>
<td>2.65 (0.04)</td>
</tr>
<tr>
<td>N</td>
<td>0 (0)</td>
<td>0.97 (0.03)</td>
</tr>
<tr>
<td>O</td>
<td>51.63</td>
<td>23.27</td>
</tr>
<tr>
<td>C/H</td>
<td>6.02</td>
<td>27.59</td>
</tr>
</tbody>
</table>

100\textsuperscript{d} 17\textsuperscript{d} 12\textsuperscript{d}

\textsuperscript{a} Based on mass of residue.
\textsuperscript{b} Based on mass of initial dry rayon.
\textsuperscript{c} Numbers in parentheses are standard deviations ($\sigma_{\text{pm}}$).
\textsuperscript{d} Mass ratio of residue to initial dry rayon, in wt%.

Units: in wt% for C, H, N, O; in wt/wt for C/H ratio.

The lab-scale apparatus and detailed description of experimental procedures for collecting the pyrolysis products of rayon are the same as those of the previous studies (Chang et al., 2000; Shie et al., 2001; Shie et al., 2002a). Several duplicate experimental runs are performed in order to collect a suitable amount of residues for analysis. The heating rate employed for the analysis of pyrolysis residues is 5K/min. The mass of rayon used for the experiments studying the pyrolysis residue is 500 ± 0.5 mg. The elemental analyses for the solid residues are made on a Perkin-Elmer, Norwalk, CT 2400 elemental analyzer with 0.3 wt% accuracy. The elements of C, H, and N are analyzed with Heraeus CHN-O-RAPID.

**RESULTS AND DISCUSSION**

**Effects of heating rate and temperature on pyrolysis of rayon**

The residual mass fraction ($M$) of rayon during pyrolysis is expressed on a normalized basis as

$$M = \frac{W}{W_0},$$

where $W$ and $W_0$ are the present and initial masses of sample, respectively. The variation of $M$ with reaction temperature ($T$) is illustrated in Fig. 2. The results indicate that a higher heating rate gives a higher value of $M$ and thus a lower yield of volatiles $V$ denoted as $M$, with $M = W_0/W_0 = 1 - M$, where $W_0$ and $M$, are the mass and mass fraction of volatiles $V$. The pyrolytic reaction is significant in 600-700K. Elemental analyses are performed in this study to analyze the solid residues at the final finished temperatures of 700K and 800K. From the data of Table 1, the molecular formula of residual mass at 700K and 800K are $\text{CH}_{0.44}\text{O}_{0.24}\text{N}_{0.01}$ with the H/C mole ratio of 0.44 and $\text{CH}_{0.31}\text{O}_{0.04}\text{N}_{0.01}$ with the H/C mole ratio of 0.31, respectively. Comparing the molecular formula of the initial rayon sample of $\text{CH}_{1.99}\text{O}_{0.93}$ with the H/C mole ratio of 1.99 with those of solid residues at 700K and 800K and noting the residual mass percentages listed in Table 1, one sees that the mole ratios of H/C of initial rayon are greater than those of samples at 700K and 800K. The scanning electrostatic microscope (SEM) photographs of front (50 and 1000
Fig. 2. Comparison of residual mass ratio \( (M) \) predicted by proposed pyrolysis model of rayon with experimental data at various heating rates \( (\beta) \). (\( \Delta \)) 1: \( \beta = 5\)K/min; (\( \times \)) 2: \( \beta = 12\)K/min; (\( \square \)) 3: \( \beta = 20\)K/min. Line: computed. Symbol: experimental. \( R_1^2, R_2^2, R_3^2 \approx 0.9936, 0.9937, 0.9949 \).

times) and back sides (50 times) of original rayon, and of pyrolysis residues of rayon at 700K and 800K are presented at Figs. 3(a), 3(b), and 3(c), and at Figs. 4(a) and 4(b), respectively. The surfaces of pyrolysis residues of rayon still remain as smooth fiber types at 700K and 800K, however, the color is changed from white to black. Therefore, it needs more vigorous activation process for the purposes of preparation of porous activated carbon. Meanwhile, the results indicate that the adsorption amounts of nitrogen on the pyrolysis residues are 0.97 and 1.05\% based on the mass of residues at 700K and 800K, respectively. Further, it apparently appears that carbon is appeared during pyrolysis process by comparing the SEM micrographs of original rayon and its pyrolytic residues shown in Figs. 3 and 4, respectively. Also from Table 1, the weight fractions of C and H of rayon reduce from 41.49 and 6.89 to 12.43 and 0.45 at 700K, and to 10.99 and 0.29 at 800K, respectively. Therefore, both carbon devolatilization and dehydration take place in the pyrolysis of rayon.

The variation of instantaneous reaction rate of yield of volatiles \( (r = dM_v/\text{dt}) \) with temperature under the three heating rates is presented in Fig. 5. The peak rates can be identified from the rate curves. For instance, the peaks occur at about 638, 651, and 663K with reaction rates of about 0.002178, 0.004554, and 0.00684 s\(^{-1}\) for heating rates of 5, 12, and 20K/min, respectively. A higher heating rate results in a higher peak value of reaction rate and a higher temperature for its occurrence.

**Kinetic parameters**

**Kinetic model**

Due to the complicated reactions of pyrolysis of rayon, many products which include the volatiles and char as noted in the experiments, may be produced, and the pyrolysis would be composed of many competitive sub-reactions. For simple engineering use, these volatile products of sub-reactions may be lumped as a pseudo-compound \( (V) \). The formation of char \( (C) \) during the pyrolysis of rayon may be attributed to the competitive formation reaction. Thus, one may reasonably adopt a two-competitive-reaction kinetic model to represent the pyrolysis of rayon as:

\[
\begin{align*}
\text{Rayon (M)} & \xrightleftharpoons[k_1]{k_2} \text{Volatile (V) (M_v)} \\
& \xrightarrow[k_2]{k_2} \text{Char (C) (M_c)}
\end{align*}
\]

In the above reaction scheme, \( M_v = W_v/W_o \) and \( M_c = W_c/W_o \), where \( W_v \) and \( W_o \), and \( M_v \) and \( M_c \) are masses, and mass fractions of residual rayon and char, respectively. According to the conservation of mass,
of Table 1, the values of \( M_c \) and \( M_e \) at 800K are 0.88 and 0.12, respectively. The foundation for the study of kinetic data from the mass-loss curve \((M = 1 - M_r)\) is based on the following kinetic reaction rate equation

\[
-dM / dt = dM_r / dt = k_1 f(M_r),
\]

where rate constant \( k_1 = A_1 \exp(-E_1/RT) \) and \( A_1 \) and \( E_1 \) are frequency factor and activation energy of volatiles, respectively. Substituting \( \beta = dT/dt \) gives

\[
-\frac{dM}{dr} = \frac{dM_r}{dr} = \beta \frac{dM_v}{dT} = k_1 (1 - M_v - M_c)^n.
\]

The reaction rate equation of \( M_c \) is

\[
\frac{dM_c}{dt} = \beta \frac{dM_c}{dT} = k_2 (1 - M_v - M_c)^{n_2}.
\]

In the above expressions, \( M_r \) and \( M_v \) are total mass fraction of volatiles and char after the pyrolysis, respectively. Equations (3) and (4) indicate that the formations of volatiles and char are both proportional to the residual mass other than volatiles and char, however, with different rate constants and exponents. The quantities of interest are re-written as follows:

\[
M = W/W_o = 1 - M_v = M_r + M_c,
\]

\[
M_v = W_v/W_o,
\]

\[
M_c = W_c/W_o,
\]

\[
M_e = W_e/W_o.
\]

In Eqs. (3) and (4), there are six kinetic parameters (activation energies of \( E_1 \) and \( E_2 \), reaction orders of \( n_1 \) and \( n_2 \) and frequency factors of \( A_1 \) and \( A_2 \) to be determined.

**Activation energy**

The differential, iso-conversion method for determining the activation energy of \( E_1 \) is employed in this study. Taking natural logarithm of Eq. (2), one obtains

\[
\ln(dM_r/dt) = \ln[A_1 f(M_r)] + (-E_1/R)(1/T).
\]

At the same \( M \) (= 1 - \( M_r \)), the reaction temperatures corresponding to the various heating rates with specific \( M \) are obtained from Fig. 2. Meanwhile, the instantaneous reaction rates of yields of volatiles corresponding to the reaction temperatures can be deduced from Fig. 5. A straight line with slope \(-E_1/RT\) is obtained by plotting \( \ln(dM_r/dt) \) vs. \( 1/T \) for every \( M \). The activation energy corresponding to the selected \( M \) can be obtained according to...
method of Friedman (1965). The activation energies under various conversions are shown in Fig. 6. The results indicate that the values of \( E_i \) for the pyrolysis of rayon are in the range of 150.2 to 214.78 kJ/mol for yields \( M_v \) ranging from 0 to 0.88. By taking the arithmetic mean of activation energies for the pyrolysis of rayon at the range of \( M_v = 0-0.88 \) (final volatile formation fraction at 800K) yielding average activation energy of 171.6 kJ/mol. Therefore, the activation energy of volatile formation of \( E_i \) is taken as 171.6 kJ/mol. The activation energy of 171.6 kJ/mol of volatile formation from the pyrolysis of rayon is comparable to those of 150-250 kJ/mol for the pyrolysis of cellulose materials (Conesa et al., 1995; Devallencourt et al., 1996; Huang et al., 1998; Yuanwen et al., 1998). The activation energy of char formation (\( E_c \)) is related to \( M_c \), which can not be identified from the TG information of \( M \) including \( M_v \) and \( M_c \). Therefore, there is no direct method to obtain the value of \( E_c \) from the data of \( M \). However, one can indirectly get a reasonable value of \( E_c \) using the iteration method as described in the latter section.

**Reaction order and frequency factor**

The order of volatile formation reaction (\( n_v \)) from the pyrolysis of rayon can be assumed as that from the pyrolysis of cellulose materials of first order (\( n = 1 \)) (Conesa et al., 1995; Devallencourt et al., 1996; Huang and Li, 1998; Yuanwen and Dillimore, 1998). The reaction order of \( n_v \) of char formation from the pyrolysis of rayon can be assumed as 1.5 similar to the char formation from the pyrolysis of PVC (Stromberg et al., 1959; Wu et al., 1994) and of PVA (Shie et al., 2002b). The referred papers pointed out that the free radical chain reactions may be the principal termination steps in char formation. Referring to the same studies, the frequency factor of char formation (\( A_2 \)) from the pyrolysis of rayon also can be assumed as \( 5.6 \times 10^{12} \) s\(^{-1} \) as that from the pyrolysis of PVC and PVA (Stromberg et al., 1959; Wu et al., 1994; Shie et al., 2002b). As for the frequency factor of volatile formation (\( A_1 \)) from the pyrolysis of rayon which is also related to \( M_v \), again, there is no direct method to obtain \( A_1 \) from data of \( M \). An iteration method can then be employed to estimate a reasonable value of \( A_1 \) as noted below.

**Estimation of \( E_c \) and \( A_1 \) and simulation results**

For the comparison of proposed model with experimental data, one needs to have the values of \( M_v \) and \( M_c \) at the various \( T (= 400-800K) \). The lose-mass fraction of pyrolysis of rayon gives \( M_v (= 1 - M) \). The production rates of \( V \) and \( C \) from Eqs. (3) and (4) can be expressed as

\[
\frac{dM_v}{dt} = \beta_1 \frac{dM_c}{dT} = A_1 \exp\left(-\frac{E_1}{RT}\right)(1-M_v-M_c)^n_v, \tag{10}
\]

\[
\frac{dM_c}{dt} = \beta_1 \frac{dM_v}{dT} = A_2 \exp\left(-\frac{E_2}{RT}\right)(1-M_v-M_c)^n_c. \tag{11}
\]

The initial conditions are

\[
M_v = 1, \ M_c = 0, \ \text{at} \ t = 0 \ (T = 400K). \tag{12}
\]

Because the constant heating rate is employed, Eqs. (10) and (11) can be solved by a forward finite difference method with the following equations.

\[
M_v(T + \Delta T) = M_v(T) + \Delta T \times \beta^{-1} \times A_1 \exp\left(-\frac{E_1}{RT}\right)\left[1 - M_v(T) - M_c(T)\right]^n_v, \tag{13}
\]

\[
M_c(T + \Delta T) = M_c(T) + \Delta T \times \beta^{-1} \times A_2 \exp\left(-\frac{E_2}{RT}\right)\left[1 - M_v(T) - M_c(T)\right]^n_c. \tag{14}
\]

The values of parameters of \( E_1, n_v, n_c \), and \( A_2 \) are obtained or estimated in the previous sections as 171.6 kJ/mol, 1, 1.5, and \( 5.6 \times 10^{12} \) s\(^{-1} \), respectively. The other parameters, \( E_2 \) and \( A_1 \) are obtained by curve fitting with the results listed in Table 2. From Table 2, the values of \( E_2 \) and \( A_1 \) with the highest value of average coefficients of determination (\( R^2 \)) at three various values of \( \beta \) (5, 12, and 20K/min) are 191.8 kJ/mol and \( 4.3 \times 10^{11} \) s\(^{-1} \), respectively. For further identifying and refining the used value of frequency factor of \( A_2 \), the curve fitting results of various \( A_2 \) values are listed in Table 3. The results indicate that the original assumed value of \( A_2 \) (5.6 \( \times \) 10\(^{12} \) s\(^{-1} \)) gives the best simulation result. Unquestioningly, \( A_2 \) of \( 5.6 \times 10^{12} \) s\(^{-1} \) is the best acceptable value. Finally, the parameters of the proposed two-competitive-reaction kinetic model for describing the pyrolysis of rayon are listed in Table 4. A comparison of residual mass fractions predicted by

![Fig. 6. Activation energy \( E_i \) vs. yield of volatile \( M_v \) for pyrolysis of rayon at heating rates of 5, 12, 20K/min, according to method of Friedman (1965).](image-url)
The proposed model with those obtained by experiments is shown in Fig. 2, indicating satisfactory agreement. To verify the applicability of kinetic parameters and the validity of the proposed model, the coefficient of determination is examined for the range of 0.05 < M < 0.85. The values of $R^2$ are 0.9936, 0.9937, and 0.9949 for the heating rates of 5, 12, and 20K/min, respectively. This supports the validity and practical applicability of the proposed simple two-competitive-reactions kinetic model for describing the pyrolysis of rayon without specifying the detailed chemical reactions involved. This supports the validity and practical applicability of the proposed simple two-competitive-reactions kinetic model for describing the pyrolysis of rayon without specifying the detailed chemical reactions involved. It is noted that Liu et al. (2003) had studied the pyrolysis of rayon in argon instead of nitrogen. Also, the rayon used by them was prewashed by warm distilled water. Further, the compositions of rayon from various sources may be different. Thus, due to these reasons, the direct comparison of their results with ours, which does not seem appropriate, are not made.

From Fig. 2, it is noted that different heating rates result in the similar masses of char formed after 700K, indicating that heating rate obviously does not affect the final production of char ($M_c = 0.17, 0.18$, and 0.18 at 700K for $\beta = 5, 12, 20K/min$, respectively). The reaction order of $n_1, n_2$ of 1.5 indicates that the free radical chain reactions may be the principal termination steps to give an overall reaction of reaction 2 (Stromberg et al., 1959; Wu et al., 1994; Shie et al., 2002b). The obtained kinetic parameters can be used to solve for Eqs. (13)-(14) to get the product yield distributions of $M_p$ and $M_c$ in the examined temperature range. The predicted product distributions ($M_p$, $M_c$, and $M$ with $M = 1 - M_c$) at the heating rate of 5K/min are shown in Fig. 7. The kinetic parameters proposed in this study have good simulation results.

### Table 2. Average coefficient of determination ($R^2$) of $A_1$ and $E_2$ by iteration method for pyrolysis of rayon.

<table>
<thead>
<tr>
<th>$A_1 \times 10^{12}$ (s⁻¹)</th>
<th>6</th>
<th>5</th>
<th>4.7</th>
<th>4.6</th>
<th>4.5</th>
<th>4.4</th>
<th>4.3</th>
<th>4.2</th>
<th>4.1</th>
<th>4</th>
<th>3</th>
</tr>
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<tbody>
<tr>
<td>$E_2$ (kJ/mol) $R^2$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>190.3</td>
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<td>0.9923</td>
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<td>0.9900</td>
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<td>190.5</td>
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<td>0.9923</td>
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<td>0.9909</td>
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</table>

### Table 3. Coefficient of determination ($R^2$) of $A_2$ refined by iteration method for pyrolysis of rayon.

<table>
<thead>
<tr>
<th>$A_2 \times 10^{12}$ (s⁻¹)</th>
<th>5K/min</th>
<th>12K/min</th>
<th>20K/min</th>
<th>Average</th>
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### Table 4. Kinetic parameters of pyrolysis of rayon.

<table>
<thead>
<tr>
<th>Activation energy $E_1, E_2$ (kJ/mol)</th>
<th>Volatile Formation</th>
<th>Char Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>171.6</td>
<td></td>
<td>191.8</td>
</tr>
<tr>
<td>Frequency factor $A_1, A_2$ (s⁻¹)</td>
<td>4.3 × 10¹¹</td>
<td>5.6 × 10¹²</td>
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<td>Reaction order $n_1, n_2$</td>
<td>1</td>
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</table>
CONCLUSION

The pyrolysis of rayon is carried out by a TGA reaction system in nitrogen atmosphere. A two-competitive-reaction kinetic model is proposed to predict the experimental results. The two competitive (parallel) reactions correspond to the formation of volatiles and char, respectively. The activation energies, frequency factors and reaction orders are determined for these two competitive reactions under experimental conditions. This study greatly assists the resource recovery of rayon as an energy resource and new carbon sources.

NOMENCLATURE

- $A$ frequency factor, s$^{-1}$
- $A_1$ frequency factor of volatile, s$^{-1}$
- $A_2$ frequency factor of char, s$^{-1}$
- $E$ activation energy, kJ/mol
- $E_1$ activation energy of volatile, kJ/mol
- $E_2$ activation energy of char, kJ/mol
- $k_1, k_2$ Arrhenius rate constant of two-competitive-reaction kinetic model,
  \[ k = A \exp \left( -\frac{E_1}{RT} \right) \]
- $n$ reaction order
- $n_1$ reaction order of volatile
- $n_2$ reaction order of char
- $M$ residual mass fraction
- $M_v$ mass fraction of volatile
- $M_r$ mass fraction of residue (rayon)
- $M_i$ mass fraction of volatile
- $R$ universal gas constant, kJ/mol-K
- $R^2$ coefficients of determination
- $r$ instantaneous reaction rate, s$^{-1}$
- $T$ temperature, K
- $t$ reaction time, s
- $W$ present mass of sample, mg
- $W_c$ mass of char, mg
- $W_{cf}$ mass of char to initial dry rayon at 800K, mg
- $W_i$ initial mass of sample, mg
- $W_r$ mass of residue (rayon), mg
- $W_v$ mass of volatile, mg

Greek symbol

- $\beta$ temperature-programmed constant heating rate, K/min

Acronyms

- ACF activated carbon fiber
- DTG differential thermogravimetric
REFERENCES


Rayon 熱裂解資源回收—動力學研究

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摘 要

Rayon 是天然生質纖維所衍生而廣泛使用於商業、工業和工程生產，特別是衣料生產，由纖維工業及消費者所產生的 rayon 在廢棄物中佔有很大的部份，將 rayon 轉化為有用的物質，如低分子量有機物、碳纖維或活性碳，不只可以解決廢棄物處理問題，更可以增加資源的再利用。在考量熱處理再利用 rayon 之前，必須先研究其熱處理時的反應動力學。本研究利用重力分析儀進行 rayon 熱裂解研究。Rayon 在反應溫度 378-800K 及升溫速率 5、12、20K/min 下，其熱裂解反應動力式可以以二競爭（並聯）反應模式反應動力模式來表示其揮發物及焦炭的產生行。其熱裂解反應動力模式參數可分別表示為：活化能 $E$ 171.6 和 191.8 kJ/mol；反應級數 $n$，1 和 1.5；及頻率因子 $A$，$4.3 \times 10^{11}$ 和 $5.6 \times 10^{12} \text{s}^{-1}$。這些資訊可以提供作為 rayon 熱裂解系統設計時之參考。