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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 (β) 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 4.3×10^{11} and 5.6×10^{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; Yuanwen and Dillimore., 1998). Also, Liu *et al.* (2003) investigated the thermal pyrolysis behaviors of two types of rayon fibers derived from wood pulp and

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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} and 1.78×10^{21} 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 viscous rayon fabric with different chemicals modified the pyrolysis process. Highest increase in yield corresponded to $AlCl_3$ and H_3PO_4. H_3PO_4 developed the widest microporosity, while Na_2HPO_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 peroxydisulphate and peroxomonosulphate 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 (β) 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-Harng 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 $CH_{1.99}O_{0.93}$ with the H/C mole ratio of 1.99.

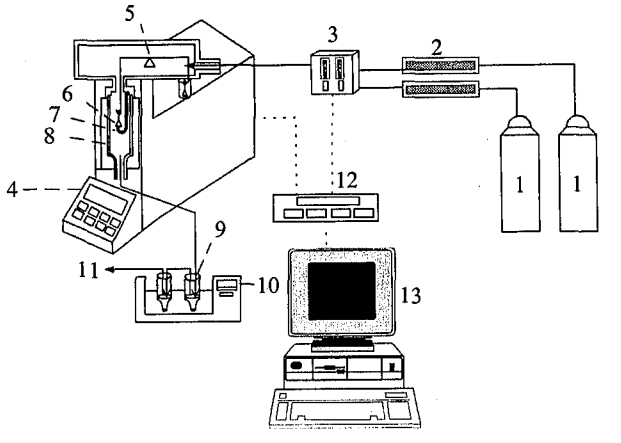
Thermogravimetry

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 (β) = 5K/min.

	Dry Rayon	700K		800K	
		a	b	a	b
C	41.49 (0.11)[c]	73.11 (1.04)	12.43	91.56 (0.11)	10.99
H	6.89 (0.05)	2.65 (0.04)	0.45	2.38 (0.25)	0.29
N	0 (0)	0.97 (0.03)	0.16	1.05 (0.06)	0.13
O	51.63	23.27	3.96	5.05	0.61
C/H	6.02	27.59		38.47	
	100[d]		17[d]		12[d]

[a] Based on mass of residue.
[b] Based on mass of initial dry rayon.
[c] Numbers in parentheses are standard deviations (σ_{n-1}).
[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.



1. Nitrogen
2. Molecular sieve
3. Flow meter
4. Control board
5. Electrobalance
6. Sample disk
7. Thermocouples
8. Furnace
9. Condenser tubes
10. Constant temperature bath
11. to sample bag
12. Data acquisition
13. Personal computer

Fig. 1. Schematic diagram of apparatus for pyrolysis experiment (Shie *et al.*, 2002b).

are in 373-1073K and controlled by a chromel-alumel thermocouple placed 1-2 mm below the Pt sample pan. The constant heating rates (β) used in this study are 5, 12, and 20K/min, respectively. The nitrogen gas with a known flow rate (*e.g.*, 30 cm^3/min at 101 kPa (1 atm) and 293K) is first introduced into the balance mechanism and then to the furnace reaction tube for at least 2 h for purging purposes. After 2 h, the furnace unit is set at a specific heating rate (5, 12, and 20K/min). Meanwhile, the data acquisition unit, with sampling intervals of 1 s, is processing throughout the entire run. The effluent gas is cold-trapped at 298K and then collected by a sample bag or vented to a fume hood. When the run is finished, the nitrogen gas is kept flowing till the temperature of the system is below 373K.

Sampling and elemental analysis

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

$$M = W / W_o , \quad (1)$$

where W and W_o 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_v with $M_v = W_v / W_o = 1 - M$, where W_v and M_v 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 $CH_{0.44}O_{0.24}N_{0.01}$ with the H/C mole ratio of 0.44 and $CH_{0.31}O_{0.04}N_{0.01}$ with the H/C mole ratio of 0.31, respectively. Comparing the molecular formula of the initial rayon sample of $CH_{1.99}O_{0.93}$ 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

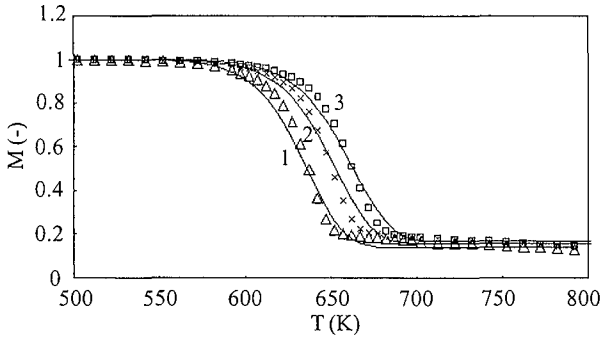


Fig. 2. Comparison of residual mass ratio (M) predicted by proposed pyrolysis model of rayon with experimental data at various heating rates (β). (Δ) 1: β = 5K/min; , ($\times$) 2: β = 12K/min; ($\square$) 3: β = 20K/min. Line: computed. Symbol: experimental. R_1^2, R_2^2, R_3^2 = 0.9936, 0.9937, 0.9949.

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 ($r = dM_v/dt$) 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,

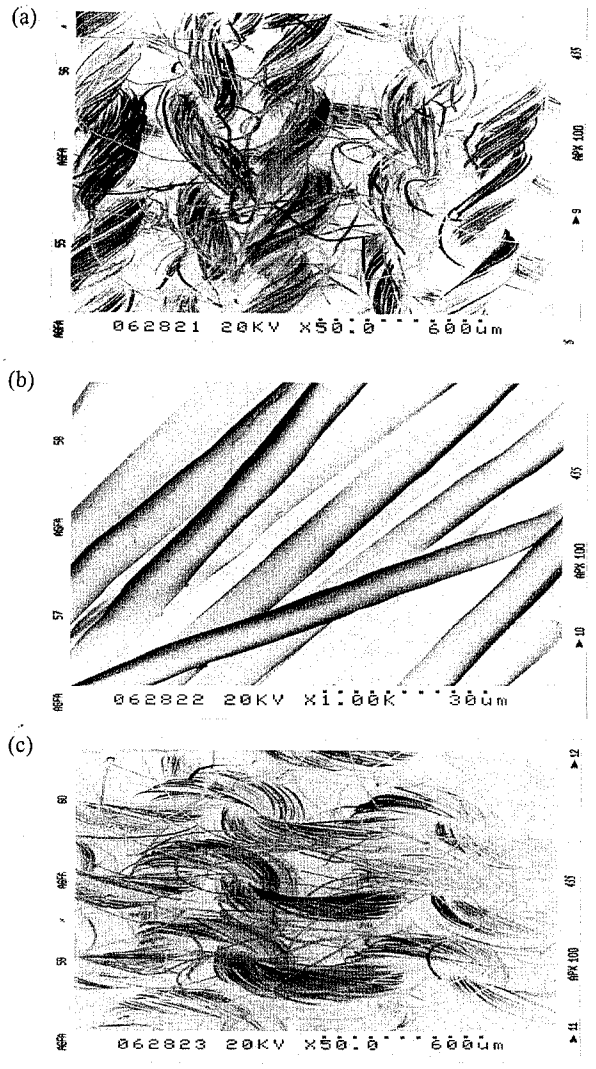
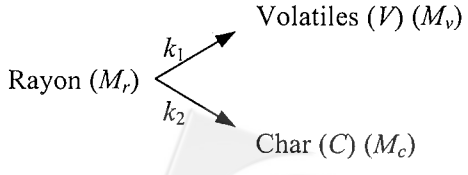


Fig. 3. The SEM micrographs of original rayon: (a) front side of 50 times; (b) front side of 1000 times; (c) back side of 50 times.

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:



In the above reaction scheme, $M_r = W_r/W_o$ and $M_c = W_c/W_o$, where W_r and W_c, and M_r and M_c are masses, and mass fractions of residual rayon and char, respectively. According to the conservation of mass,

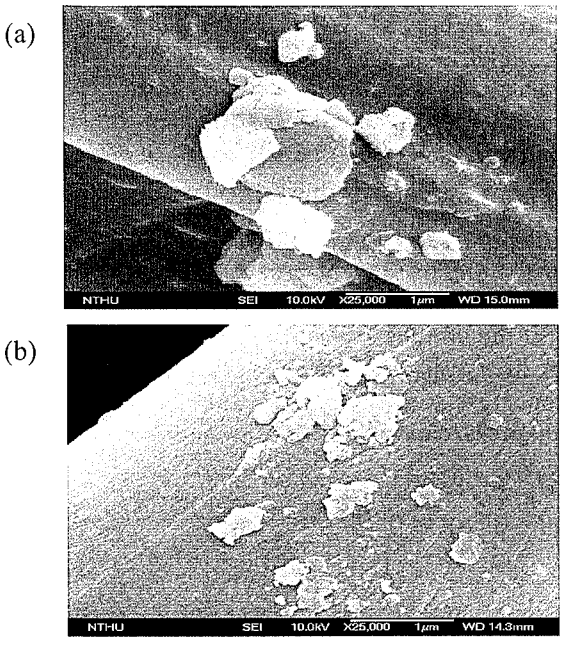


Fig. 4. The SEM micrographs of rayon residues after being pyrolyzed to various temperatures: (a) 700K; (b) 800K.

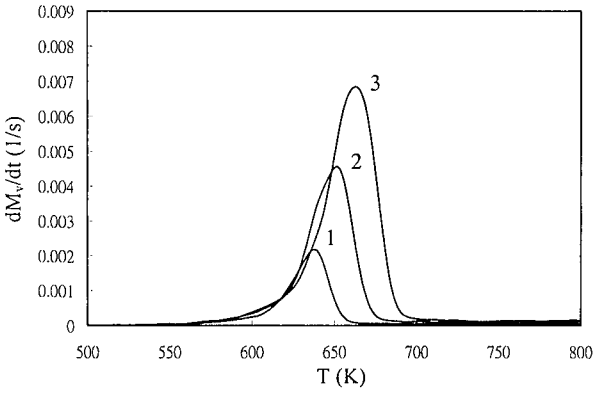


Fig. 5. Variation of instantaneous reaction rate of yield of volatiles r (= dM_v/dt) with temperature T at different heating rates for pyrolysis of rayon in nitrogen. Other notations are the same as those specified in Fig. 2.

$W_r = W_o - W_v - W_c$, or $W_o = W_r + W_v + W_c$. Dividing by W_o gives $1 = M_r + M_v + M_c$.

According to the two-competitive-reaction pyrolysis model and Arrhenius law, the solutions of W/W_o (= M = 1 – M_v), W_v/W_o (= M_v) and W_c/W_o (= M_c) can then be solved. From Table 1, the ratio of char to initial dry rayon at 800K, denoted as W_{cf}/W_o, is about 0.11, which is close to that of residue to initial dry rayon (M) of about 0.12, indicating that the residue contains almost the char at 800K. Here, W_{cf} denotes the mass of char at 800K.

For the pyrolysis reaction with T = 400-800K, $M_v = (W_o - W_{cf})/W_o$ and $M_c = W_{cf}/W_o$ at 800K while $M_v = M_c = 0$ at T = 400K. Therefore, from the results of Table 1, the values of M_v and M_c at 800K are 0.88 and 0.12, respectively. The foundation for the study of kinetic data from the mass-loss curve ($M = 1 - M_v$) is based on the following kinetic reaction rate equation

$$-dM/dt = dM_v/dt = k_1 f(M_v), \quad (2)$$

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

$$-\frac{dM}{dt} = \frac{dM_v}{dt} = \beta\frac{dM_v}{dT} = k_1(1 - M_v - M_c)^{n_1}. \quad (3)$$

The reaction rate equation of M_c is

$$\frac{dM_c}{dt} = \beta\frac{dM_c}{dT} = k_2(1 - M_v - M_c)^{n_2}. \quad (4)$$

In the above expressions, M_v and M_c are total masses 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:

$$M = W/W_o = 1 - M_v = M_r + M_c, \quad (5)$$

$$M_v = W_v/W_o, \quad (6)$$

$$M_c = W_c/W_o, \quad (7)$$

$$M_r = W_r/W_o. \quad (8)$$

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

$$\ln(dM_v/dt) = \ln[A_1 f(M_v)] + (-E_1/R)(1/T). \quad (9)$$

At the same M (= 1 – M_v), 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_v/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_1 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_1 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 cellulosic materials (Conesa *et al.*, 1995; Devallencourt *et al.*, 1996; Huang *et al.*, 1998; Yuanwen *et al.*, 1998). The activation energy of char formation (E_2) is related to M_c, which can not be identified from the TG information of M including M_c and M_r. Therefore, there is no direct method to obtain the value of E_2 from the data of M. However, one can indirectly get a reasonable value of E_2 using the iteration method as described in the latter section.

Reaction order and frequency factor

The order of volatile formation reaction (n_1) from the pyrolysis of rayon can be assumed as that from the pyrolysis of cellulosic 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_2 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 5.6×10^{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_c, 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.

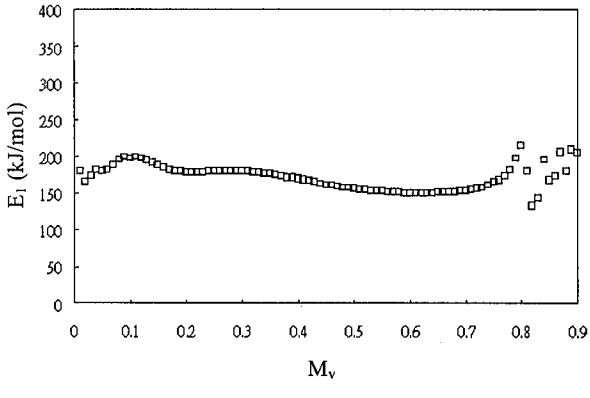


Fig. 6. Activation energy E_1 vs. yield of volatile M_v for pyrolysis of rayon at heating rates of 5, 12, 20K/min, according to method of Friedman (1965).

Estimation of E_2 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

$$\frac{dM_v}{dt} = \beta \frac{dM_v}{dT} = A_1 \exp(-E_1 / RT)(1 - M_v - M_c)^{n_1}, \tag{10}$$

$$\frac{dM_c}{dt} = \beta \frac{dM_c}{dT} = A_2 \exp(-E_2 / RT)(1 - M_v - M_c)^{n_2}. \tag{11}$$

The initial conditions are

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

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

$$M_v(T + \Delta T) = M_v(T) + \Delta T \times \beta^{-1} \times A_1 \exp(-E_1 / RT)[(1 - M_v(T) - M_c(T)]^{n_1}, \tag{13}$$

$$M_c(T + \Delta T) = M_c(T) + \Delta T \times \beta^{-1} \times A_2 \exp(-E_2 / RT)[1 - M_v(T) - M_c(T)]^{n_2}. \tag{14}$$

The values of parameters of E_1, n_1, n_2, and A_2 are obtained or estimated in the previous sections as 171.6 kJ/mol, 1, 1.5, and 5.6×10^{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 β (5, 12, and 20K/min) are 191.8 kJ/mol and 4.3×10^{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 (5.6×10^{12} s^{-1}) gives the best simulation result. Unquestionably, A_2 of 5.6×10^{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

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

E_2 (KJ/mol) \ $A_1 \times 10^{11}$ (s^{-1})	6	5	4.7	4.6	4.5	4.4	4.3	4.2	4.1	4	3
190.3	–	0.9912	0.9923	–	0.9915	–	0.9900	–	–	0.9845	–
190.5	–	–	0.9925	–	0.9923	–	0.9909	–	–	0.9863	–
190.8	0.9748	0.9931	0.9930	–	0.9932	–	0.9924	–	–	0.9886	0.9464
191	–	0.9908	0.9931	–	0.9935	–	0.9930	–	–	0.9898	–
191.3	–	–	–	0.9935	0.9937	0.9938	0.9937	0.9932	–	–	–
191.4	–	–	–	0.9934	0.9938	0.9939	0.9938	0.9934	–	–	–
191.5	–	0.9896	0.9927	0.9933	0.9938	0.9939	0.9939	0.9936	–	0.9920	–
191.6	–	–	–	0.9932	0.9938	0.9940	0.9940	0.9938	0.9932	0.9925	–
191.7	–	–	–	0.9930	0.9936	0.9939	0.9940	0.9939	0.9934	0.9927	–
191.8	–	–	–	0.9929	0.9935	0.9939	**0.9941**	0.9940	0.9936	0.9929	–
191.9	–	–	–	0.9927	0.9934	0.9938	0.9940	0.9940	0.9937	0.9931	–
192	–	–	–	0.9924	0.9931	0.9937	0.9939	0.9940	0.9936	0.9932	–
192.1	–	–	–	0.9923	0.9930	0.9936	0.9939	0.9940	0.9938	0.9933	–
192.2	–	–	–	0.9920	0.9928	0.9934	0.9938	0.9940	0.9938	0.9934	–

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

$A_2 \times 10^{12}$ (s^{-1})	Coefficient of Determination (R^2)			
	5K/min	12K/min	20K/min	Average
5	0.9912	0.9933	0.995	0.9932
5.1	0.9916	0.9934	0.9952	0.9934
5.2	0.9919	0.9935	0.9952	0.9935
5.3	0.9922	0.9936	0.9952	0.9937
5.4	0.9925	0.9937	0.9951	0.9938
5.5	0.9927	0.9937	0.9951	0.9938
5.6	**0.9936**	**0.9937**	**0.9949**	**0.9941**
5.7	0.9931	0.9937	0.9948	0.9939
5.8	0.9933	0.9936	0.9946	0.9938
5.9	0.9935	0.9936	0.9943	0.9938
6	0.9936	0.9934	0.9941	0.9937
6.5	0.994	0.9923	0.9923	0.9929
7	0.9938	0.9905	0.9897	0.9913

Table 4. Kinetic parameters of pyrolysis of rayon.

	Pyrolysis Reactions	
	Volatile Formation	Char Formation
Activation energy E_1, E_2 (kJ/mol)	171.6	191.8
Frequency factor A_1, A_2 (s^{-1})	4.3×10^{11}	5.6×10^{12}
Reaction order n_1, n_2	1	1.5

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 pro posed 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 finial production of char (M_c = 0.17, 0.18, and 0.18 at 700K for β = 5, 12, 20K/min, respectively). The reaction order of 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_v and M_c in the examined temperature range. The predicted product distributions (M_v, M_c, and M with $M = 1 - M_v$) at the heating rate of 5K/min are shown in Fig. 7. The kinetic parameters proposed in this study have good simulation results.

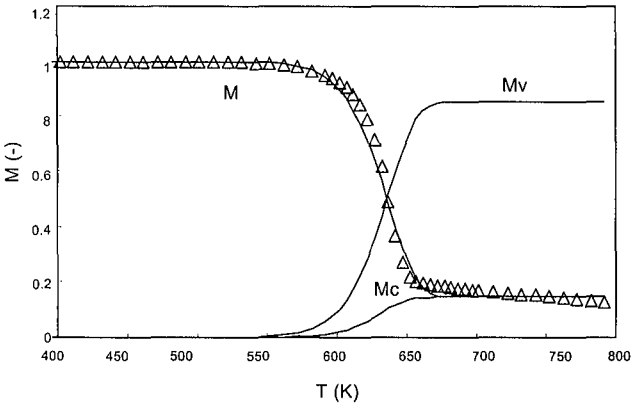


Fig. 7. Computed values from proposed model and experimental data of mass fraction of solid (M), and computed values of mass fractions of volatiles (M_v) and char (M_c) for pyrolysis of rayon at heating rate of 5K/min. Line: computed. Symbol (Δ): experimental.

Implication of kinetic models and variation with heating rates

The two-competitive-reaction kinetic model proposed herein for the pyrolysis of rayon is simple for the engineering use. The detailed intrinsic reaction scheme should be rather complex and would need further study to elucidate it.

Further from this study, a higher heating rate gives a higher value of the residue mass fraction at the same reaction temperature and thus a lower volatile formation. A higher heating rate also results in a higher peak value of reaction rate of volatile formation and a higher temperature for its occurrence. For the rayon initially subjected to a high temperature (say 800K), one may regard the situation as a special case of employing extremely high heating rate with a set ceiling temperature. Thus, according to the two-competitive-reaction kinetic model and the role of heating rate on yield and reaction rate of volatile formation, the product spectrum would be different for the cases with different heating rates and pre-set ceiling temperatures. Hence, the proposed kinetic model provides useful information for the proper design and operation of the pyrolysis system of rayon.

Kinetic studies are often performed by nonisothermal thermogravimetric analysis (TGA). Obviously, it is difficult to distinguish the mass signal versus time or temperature into complex reaction systems (Boldyreva, 1987). Nevertheless, TGA data can still provide essential knowledge for establishing the kinetic expressions of formation of volatiles as a whole and of char for the technical and engineering purpose.

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, $k = A \exp(-E/RT)$
n	reaction order
n_1	reaction order of volatile
n_2	reaction order of char
M	residual mass fraction
M_c	mass fraction of char
M_r	mass fraction of residue (rayon)
M_v	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_o	initial mass of sample, mg
W_r	mass of residue (rayon), mg
W_v	mass of volatile, mg

Greek symbol

β	temperature-programmed constant heating rate, K/min

Acronyms

ACF	activated carbon fiber
DTG	differential thermogravimetric

DR	Dubinin-Radushkevich
MEK	methyl-ethyl-ketone
TG	thermogravimetric
TGA	thermogravimetric analysis
SEM	scanning electrostatic microscope

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Rayon 熱裂解資源回收—動力學研究

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摘　要

Rayon 是由天然生質纖維所衍生而廣泛使用於商業、工業和工程生產，特別是衣服生產。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 轉化爲有用的物質，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行爲。本研究利用熱重分析儀進行 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) 反應型反應動力模式來表示其揮發物及焦炭的產生行爲。其熱裂解之反應動力模式參數可分別表示爲：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，4.3×10^{11} 和 $5.6 \times 10^{12}\ s^{-1}$。這些資訊可以提供作爲 rayon 熱裂解系統設計時之參考。