Two-Step Consecutive Reaction Model and Kinetic Parameters Relevant to the Decomposition of Chinese Forest Fuels

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ABSTRACT: Decomposition of some Chinese forest fuels has been studied by means of nonisothermal thermogravimetric analysis in oxidative and inert atmosphere at low heating rates. A comparison between thermogravimetric curves obtained in air and nitrogen shows that the existence of oxygen enhances the decomposition rate and changes the mechanisms of thermal degradation. After the water evaporation, two well-defined decomposition stages have been observed in thermogravimetric curves obtained in air, which correspond to oxidative degradation of main components and oxidation of char formed. A kinetic model named "twostep consecutive reaction model" is developed to describe the thermal degradation process of these materials in air, and there is a good agreement between the experimental and calculated thermogravimetric and derivative thermogravimetric curves. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 571–576, 2006

Key words: forest fuels; thermal decomposition; kinetic model; kinetic parameters

INTRODUCTION

Forest fire is a global phenomenon occurring in tropical, temperate, and boreal regions. It is estimated that, at a global scale, nearly 500 million hectares are affected by fire every year, including 10-15 million hectares of boreal and temperate forest¹ in China. China is short of forestry resources, but has suffered many forest fires.² The modeling of spreading of Chinese forest fires will be of enormous help in making safety decisions in situ. As we know, although there are statistical, semiempirical, and physical approaches to simulate the forest fire spread, 3 the generation of new models tends to include more and more physicochemical mechanisms.4,5 Understanding the thermal decomposition of natural fuels and, at the same time, obtaining the kinetic parameters are of great importance for the study on the behavior of bulk biomass in fire and the modeling of natural fuel combustion and fire propagation.

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The thermal decomposition of biomass involves many different reactions because of chemical complexity. This complexity has led some researchers to study thermal pyrolysis of biomass components separately, especially those of cellulose, which have been studied at varying levels of detail by a great number of investigators,^{6–12} and detailed reviews by Milosavljevic and Suuberg,¹³ Antal and Varhegyi,¹⁴ and Antal et al.¹⁵ can be referred to. Global kinetics has also been used successfully to describe the pyrolysis of lignin and hemicellulose (for which xylan is often used as a representative).^{16–18}

As for the biomass itself, some researchers^{19–21} regarded biomass as consisting of a single pseudocomponent, and used its solid-gas reaction kinetics during the overall temperature range to describe the biomass loss kinetics in nitrogen atmosphere. Some other researchers^{8,22,23} looked on the biomass as consisting of multiple pseudocomponents. Each pseudocomponent represented a single real component or a mixture of several real components, and biomass decomposition was modeled by the superposition of the overall decompositions of these components. As for biomass decomposition in oxidative atmosphere, Haykin-Acma²⁴ investigated the combustion characteristics of some biomass samples by using nonisothermal thermogravimetry. Momoh et al.25 and Senneca et al.26 observed the two-stage mass loss process of biomass decomposition in air, and computed the kinetic parameters of each step separately. Liu et al.²⁷ developed a simple kinetic description named as "First Order

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Pseudo Bi-component Separate-Stage Model (PBSM-O1)." In this model, the sample subjected to experiment was regarded as being formed of two independent pseudocomponents, which decomposed respectively in two separate temperature regions. And, the temperature corresponding to the minimum in the derivative thermogravimetric (DTG) curve is regarded as the point of separation between two mass-loss stages. To our knowledge, the two-stage mass loss process is usually dealt with separately by using various kinetic models; however, there is relatively scarce research about the mechanism of biomass decomposition in oxidative atmosphere.

In the present work, nonisothermal TG analysis has been studied to understand the decomposition behavior of Chinese forest fuels in air atmosphere. A kinetic description suitable for biomass mass loss behavior in air under relatively low heating rate is proposed. This work is carried out as a part of the study on the behavior of bulk biomass in fire, and the low heating rate kinetics can be used in the formulation of the smoldering combustion as well as the behavior of the interior of the bulk samples in fire, where heating rates are comparable to that used in this work.

EXPERIMENTAL

The principal experimental variables that could affect the thermal decomposition characteristics in a TG analysis are the pressure, the purge gas flow rate, the heating rate, the weight of the sample, and the sample size fraction. In the present study, wood and leaf samples of some Chinese forest fuels, collected from forest zone in Jiangxi province of China, were subject to dynamical thermal decomposition experiments. After being dried for 24 h at 80°C, these materials were ground and sieved so that the particle size was specified to be less than 300 μ m. The grains of the sample were evenly distributed over the open sample pan of 5-mm diameter loosely, with the initial amounts of the samples all kept to ~ 10 mg. The depth of the sample layer filled in the pan is about 0.5 mm. Thermal decomposition was observed in terms of the overall mass loss by using a NETZSCH STA 409C Thermobalance. At the same time, a differential scanning calorimetry (DSC) curve was recorded. Temperature calibration of thermogravimetric analysis (TGA) was carried out by Curie Point Standards with special concern. An air or nitrogen stream was continuously passed into the furnace at a flow rate of 50 mL/min (at normal temperature and atmospheric pressure). The temperature was increased to 750°C at the heating rates of $10^{\circ}C/$ min for all samples. Other heating rates (for example, 5, 20°C/min) for some samples were used for more detailed investigation and comparison. For each sample, two runs were performed with the same experimental conditions, and the experiment reproducibility



Figure 1 Experimental TG and DTG curves of the oil-tea wood samples in air and nitrogen atmosphere at 5°C/min.

was verified by reasonable agreement between the two obtained mass loss curves. The DTG curves were calculated from the TG curves that were smoothed by using Gaussian smoothing method.²⁸

RESULTS AND DISCUSSION

Characteristics and comparison of biomass loss curves in nitrogen and air atmosphere

Figure 1 presents the superimposed TG and DTG curves of the oil-tea wood samples in nitrogen and air atmosphere at 5°C/min. As shown in this figure, after the moisture content is removed at lower temperature, the DTG curve in nitrogen atmosphere shows a large peak with a shoulder and a long tail. The lowertemperature shoulder may represent hemicellulose degradation, and the large peak may represent cellulose decomposition. The long tail at higher temperature may correspond to lignin decomposition, since lignin is known to decompose over a wide temperature range.^{29,30} In higher temperature range, the weight is gradually lost, and at 700°C, the overall mass remained is still 25.6%. In air atmosphere, all samples subjected to experiments are found to give the same general shape for the TG/DTG curves. The evaporation of moisture and low volatility extractive constituents occurring in the temperature range of 100-180°C constitutes an approximately 10% mass loss for all samples. Following the evaporation, the first major mass loss due to decomposition begins slowly and accelerates rapidly in the temperature range of 290–340°C. A second major mass loss follows the first one and reaches an overall mass loss of more than 90%. The two distinct DTG peaks are not completely separated. Table I shows some characteristic data from the TG curves, such as mass loss at 200°C (mainly moisture and low volatility extractive constituents content) and mass remaining at 700°C (mainly ash content).

Sample	Atmosphere	Mass loss at 200°C (%)	Mass remained at 700°C (%)	Temperature of shoulder (°C)	Temperature of Peak 1 (°C)	Temperature of Peak 2 (°C)
Oil-tea wood	Air	10.4	2.9		298	416
Oil-tea wood	N_2	10.4	25.6	292	332	_
Oil-tea leaf	Air	8.1	9.0		296	447
Oil-tea leaf	N_2	8.0	28.6	286	331	
Loquat leaf	Air	5.9	14.3		287	444
Loquat leaf	N_2	5.1	22.3	280	319	
Michelia maudiae wood	Air	9.1	6.3		298	461
Michelia maudiae leaf	Air	6	14.0	_	302	488
Chinese Gugertree wood	Air	11.6	4.4		294	458
Chinese Gugertree leaf	Air	10.9	11.0		304	456
Masson's pine wood	Air	11.0	3.3		297	436
Masson's pine leaf	Air	9.2	11.8		319	469
Chinese fir wood	Air	8.4	5.7		318	444
Chinese fir leaf	Air	8.6	11.3	_	329	466

 TABLE I

 Features of the Thermogravimetric Curves of Different Samples in Air and Nitrogen Atmosphere at 10°C/min

A comparison between TG curves obtained in air and nitrogen atmosphere shows that the hemicellulose shoulder and the cellulose peak in nitrogen merge into one big peak and occur at lower temperatures (roughly 30–35°C lower, Table I) in air. Oxygen not only enhances the decomposition of the material at low temperatures, but also is likely to promote the combustion of char residue at higher temperatures. In the absence of oxygen, the peak region is followed by a wide region of very low conversion rates, essentially as a result of lignin decomposition. While in the presence of oxygen, given the relatively high temperatures, it is possible that the activity of combustion reactions is already important. Combustion, leading to the complete conversion of the charred solid, terminates at about 600°C. When experiments in air are carried out at higher heating rates, the overall qualitative trends of DTG curves are similar to those at low heating rates. However, the second mass loss peak (for example, see Fig. 2) becomes very sharp



Figure 2 Experimental decomposition curves for Loquat leaf samples in air at a heating rate of 20°C/min.

and like a spike, indicating this mass loss process is violent. The DSC curve, which recorded heat effect of the same run of the experiment, also shows two exothermic peaks accompanied with the two mass loss peaks in Figure 2. Moreover, the second exothermic peak is very acute, since the peak value is about 10 times bigger than the corresponding peak values of the experiments at lower heating rates, making clear that the heat release is also violent. The second peaks of TG and DSC curves of Figure 2 both suggest that at high heating rates ignition may initiate and combustion may progress, while at low heating rates, slow oxidation of char is dominant.

Kinetic mechanism of the decomposition behavior of biomass in air

As stated above, there is a considerable amount of evidence existing to support the mechanism that thermal decomposition of forest fuels in air shows two stages (except of the dehydration step): oxidative degradation of main components and oxidation of char formed. The two global processes show two overlapped peaks in the DTG curves. Each step contains many simultaneous reactions, but there is no need and no possibility to model every reaction. Because of its two-stage characteristic, the decomposition of Chinese forest fuels in air would be best described by a twostep consecutive-reaction model.

This model also can be proved by some published research. Orfao et al.²² studied the decomposition behavior of cellulose, xylan, and lignin under nitrogen and air by TGA. When compared with cellulose decomposition rate in nitrogen, cellulose decomposition rate in air exhibits a second peak in higher temperature range, because of char oxidation. Hemicellulose decomposition process in air is also possible to define two zones. The rate of lignin decomposition process shows only one peak, but the processes of volatile formation and residue gasification occur simultaneously in the temperature range considered. So, the decomposition behavior of main biomass components reveals that biomass first loses its weight for pyrolysis, and then for oxidation when heating in air.

In this study, the proposed kinetic model considers a two-step consecutive reaction following the scheme:

$$k_1$$

$$S \longrightarrow a_1 R_1 + b_1 V_1$$

$$k_2(O_2)$$

$$a_1 R_1 \longrightarrow a_2 R_2 + b_2 V_2$$

where *S* is the original biomass particles, R_i and V_i are the residues, char for reaction 1 and ash for reaction 2, respectively, and the volatiles generated in reaction *i* and the yield coefficients a_1 and b_1 are expressed as grams of R_i or V_i divided by grams of reacted biomass $(S_0 - S)$, where S_0 is the initial biomass amount. If S_0 is defined as the initial mass fraction of solid and logically equals 1, *S* and R_i will be the mass fractions. The yield factor b_1 equals the maximum amount of volatiles $V_{1\infty}$ evolved by Reaction 1 and b_2 equals the maximum amount of volatiles $V_{2\infty}$ evolved by Reaction 2. And consequently a_1 equals $(1 - V_{1\infty})$ and that a_2 equals $(1 - V_{1\infty} - V_{2\infty})$.

The kinetic law could be expressed in terms of the solid weight registered at time *t*, and according to the general definition of reaction rate, the following equations can be developed:

$$\frac{d(S/S_0)}{dt} = -k_1(S/S_0)^{n_1} \tag{1}$$

$$\frac{d((R_1/S_0)/a_1)}{dt} = k_1(S/S_0)^{n_1} - k_2((R_1/S_0)/a_1)^{n_2}$$
(2)

The parameter α , considered as the conversion (reacted fraction), is defined with respect to mass fraction of solids or mass fraction of volatiles evolved as:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} = \frac{V}{V_\infty} \tag{3}$$

In the thermogravimetric experiments, the registered weight is the sum of the nonreacted sample *S* and the residues R_i formed in the reactions. To avoid the difficulty of determining the mass loss of each reaction, the following conversions are defined:

$$\alpha_i = \frac{V_i}{V_{i\infty}} \qquad i = 1, 2 \tag{4}$$

From the mass balance theory, it can be deduced that 31,32

$$\frac{S}{S_0} = 1 - \frac{V_1}{b_1} = 1 - \frac{V_1}{V_{1\infty}}$$
(5)

$$\frac{R_1}{S_0} = a_1 \frac{V_1}{b_1} - a_1 \frac{V_2}{b_2} = a \left[\frac{V_1}{V_{1\infty}} - \frac{V_2}{V_{2\infty}} \right]$$
(6)

From eqs. (1)-(6) it can be deduced that

$$\frac{d\alpha_1}{dt} = k_1 (1 - \alpha_1)^{n_1} \tag{7}$$

$$\frac{d\alpha_2}{dt} = k_2(\alpha_1 - \alpha_2)^{n_2} \tag{8}$$

The value that can be experimentally evaluated is the overall degree conversion α :

$$\alpha = \frac{w_0 - w}{w_0 - w_{\infty}} = \frac{V}{V_{\infty}} = \frac{V_1 + V_2}{V_{1\infty} + V_{2\infty}} = \frac{V_{1\infty}\alpha_1 + V_{2\infty}\alpha_2}{V_{1\infty} + V_{2\infty}}$$
(9)

$$\frac{d\alpha}{dt} = \frac{1}{V_{1\infty} + V_{2\infty}} \left(V_{1\infty} \frac{d\alpha_1}{dt} + V_{2\infty} \frac{d\alpha_2}{dt} \right)$$
(10)

The apparent kinetic parameters of each reaction can be optimized by fitting the above kinetic equations to the DTG curves at the heating rate of 10°C/min. The NETZSCH Thermokinetics program³³ was used to optimize the kinetic parameters and reaction order. As can be observed in Figure 3, there is a good agreement between the experimental and calculated TG and DTG curves.

Comparison of the kinetic model and parameters with those reported in literature

As mentioned in Introduction, there are some kinetic models to describe the moss loss behavior of lignocellulosic materials,25-27 which in common dealt with each DTG peak separately, while this study proposes a two-step consecutive-reaction model and processes the two peaks simultaneously by optimization computation. Figure 4 shows the individual contributions of the two decomposition steps to the total conversion, which the proposed model is applied to describe the conversion process of oil-tea wood sample heated in air at 10°C/min. Obviously, α_1 as well as α_2 increases with temperature, and the value of α_2 begins to be significant when the value of α_1 is already high. For example, as shown in Figure 4, $\alpha_1 = 90\%$ when α_2 = 5% at 350°C. These results indicate that the two mass loss steps do not overlap very much. As a good approximation, the decomposition of lignocellulosic materials in an oxidative atmosphere can be also modeled as the reaction of each step following indepen-



Figure 3 Experimental and fitted TG/DTG curves for oiltea wood samples at 10°C/min

dent processes. In these models, since the steps are dealt with separately, various methods of deriving kinetic parameters, other than optimization computation, can be adopted.

Table II summaries the kinetic parameters of some Chinese forest fuels for the proposed model. Comparison of the kinetic parameters obtained with those reported in the literature is not an easy task, because in most cases, there are many differences in material properties, experimental conditions, etc. In many articles, kinetic parameters of the decomposition process of lignocellulosic materials have been estimated, assuming two global reactions with *n*th-order rates. For the oxidative decomposition step, the activation energies are roughly comprised between 101 and 136,²⁵ 130²⁶, 83-93,³⁴ 78 or 121³⁵ (two computation methods), and 52–99.²⁷ For the char oxidation step, the values reported are 35-65,25 $110^{26}_{,26}$ 65–83,³⁴100 or 128,³⁵ 87–202,²⁷ and 94 kJ/mol.³⁶ Therefore, the present results agree reasonably well with those from similar studies. The reaction orders of two stages were assumed to be unity in many papers, only reaction orders of 2.8²⁶ and 2.39³⁵ were found for the first step and orders of 1.2²⁶ and 1.3³⁵ for second step. However, in Table II, the reaction order of oxidative decomposition step is higher than 1 (scattering around 1.5), and that of char oxidation step is mostly a little lower than 1. This reveals that the reaction mechanism is more complicated than the assumption of first-order reaction. Moreover, since one decomposition step contains many basic chemical reactions, there is no need to assume it follows the first-order model. The variability among the kinetic parameters and reaction orders of biomass decomposition in air can be due to differences between the

Moreover, since one decomposition step contains many basic chemical reactions, there is no need to assume it follows the first-order model. The variability among the kinetic parameters and reaction orders of biomass decomposition in air can be due to differences between the biomass species, the experimental conditions (sample size, heating rate, etc.), and the mathematical treatments of the experimental data. The effect of oxygen concentration is also needed to further investigated. Calvo et al.³⁵ listed the kinetic parameters of rice straw in the atmosphere with different oxygen concentrations, which showed the activation energy and reaction order vary greatly with the oxygen concentration. Apart from these considerations, there are also other reasons that motivate the need for further investigation.

CONCLUSIONS

Decomposition of some Chinese forest fuels has been studied by means of nonisothermal thermogravimetric analysis in oxidative atmosphere at low heating rates. After the water evaporation stage, a first stage of volatiles release has been in general observed, followed by an oxidation stage. DTG profiles recorded in air have been compared with those recorded in nitrogen. The comparison suggests that thermal decomposition is largely affected by oxidizing conditions. Moderate enhancement of the early pyrolysis stage is observed, and the pro-



Figure 4 Individual contributions of the two decomposition steps to the total conversion, which the two-step consecutive-reaction model is applied to describe the conversion process of oil-tea wood sample heated in air at 10°C/min.

TABLE II Kinetic Parameters of Some Chinese Forest Lignocellulosic Materials Decomposed in Air at 10°C/min

Sample	Reaction step	Weighting factor $rac{V_{i^{\infty}}}{V_{1^{\infty}}+V_{2^{\infty}}}$	Activation energy (kJ/mol)	Pre-exponential factor (s ⁻¹)	Reaction order
Oil-tea wood	А	0.666	101.9	1.11×10^{7}	1.7
	В	0.334	123.9	1.06×10^{9}	1.4
Oil-tea leaf	А	0.638	59.1	4.21×10^{3}	1.1
	В	0.362	148.1	1.20×10^{9}	1.1
Michelia maudiae wood	А	0.630	91.2	1.29×10^{6}	1.8
	В	0.370	80.1	1.61×10^{3}	0.7
Michelia maudiae leaf	А	0.626	60.8	1.23×10^{3}	1.5
	В	0.374	98.8	2.13×10^{4}	0.7
Chinese Gugertree wood	А	0.622	96.6	4.54×10^{6}	1.9
	В	0.378	88.5	7.76×10^{3}	0.7
Chinese Gugertree leaf	А	0.528	59.0	8.56×10^{2}	1.2
	В	0.472	71.0	3.86×10^{2}	0.6
Masson's pinewood	А	0.606	106.1	3.64×10^{7}	1.8
	В	0.394	101.3	1.12×10^{5}	0.9
Masson's pine leaf	А	0.554	79.3	5.33×10^{4}	1.6
	В	0.446	77.7	9.08×10^{2}	0.7
Chinese fir wood	А	0.683	129.2	1.68×10^{9}	1.4
	В	0.317	137.6	6.61×10^{7}	1.0
Chinese fir leaf	А	0.549	68.0	3.32×10^{3}	1.0
	В	0.451	125.0	2.96×10^{6}	1.0

(Reaction step A, $S \rightarrow a_1 R_1 + b_1 V_1$, $B: a_1 R_1 \rightarrow a_2 R_2 + b_2 V_2$).

duced char is fully oxidated by oxygen. At higher heating rates, the char may ignite and burn out.

A kinetic model, considering a two-step consecutive reaction, is proposed to describe the mass loss behavior of these samples. The two steps correspond to the oxidative pyrolysis process of main components and the oxidation of char formed. The kinetic parameters are calculated and compared with the literature, suggesting that the proposed scheme can describe the thermal decomposition process well.

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