Thermal decomposition of pine branch: Unified kinetic model on pyrolytic reactions in pyrolysis and combustion

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HIGHLIGHTS

- We present a new kinetic model of thermal decomposition of pine branch, with unified kinetic descriptions of the major pyrolytic reactions in pyrolysis and combustion.
- Consistent reaction schemes with the same proportions of pseudo-components are used to simulate the pyrolytic reactions in pyrolysis and combustion.
- Genetic Algorithm (GA) and non-linear fitting algorithm are successfully combined to evaluate the kinetic parameters.

GRAPHICAL ABSTRACT

Experimental and simulated TG and DTG curves for PB combustion in air (20 °C/min), with the contributions of the four pseudo-components. The kinetic parameters were evaluated by combined use of Genetic Algorithm (GA) and non-linear fitting algorithm.
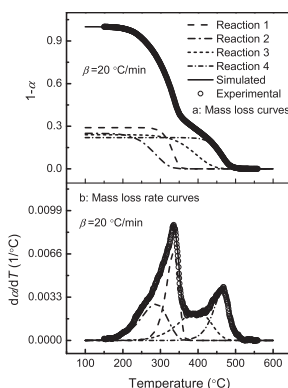
ABSTRACT

This paper presents a new kinetic model of thermal decomposition of pine branch, with unified kinetic descriptions of the major pyrolytic reactions in pyrolysis and combustion. Experiments for pine branch (PB) of *Pinus sylvestris* were performed by dynamic thermogravimetry in nitrogen and air atmospheres at heating rates of 10, 15 and 20 °C/min. The major pyrolytic mass losses in pyrolysis and combustion are interpreted as the sum of the volatilization due to consistent parallel reactions (1st order) of pseudo-components of cellulose, hemicellulose, and lignin. Consistent kinetic schemes with the same proportions of the three pseudo-components are used to simulate the pyrolytic reactions in pyrolysis and combustion. The oxidation of fixed carbon generated from the non-volatilizable component in the original material was simulated as the forth reaction in combustion. Genetic Algorithm (GA) and non-linear fitting algorithm are combined to optimize a set of kinetic parameters to fit the experimental data. The validity and reliability of the new kinetic models are verified by the good fit between the simulated and experimental derivative thermogravimetric (DTG) curves.

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1. Introduction

The study of the thermal decomposition of plant materials is of great importance in the wildland fire modeling and the fuel hazard studies, since plant pyrolysis is the fundamental step to release volatile compounds which support fuel ignition and flaming combustion. Especially, the burning of tree branch plays an important role in inducing crown fires in wildland. Plant is a typical kind of lignocellulosic material which primarily consists of cellulose, hemicellulose and lignin, and the pyrolysis products mainly include gaseous volatiles (combustible and non-combustible) and fixed carbon. In kinetic analysis, the pyrolysis of lignocellulosic material is usually interpreted as a sum of the volatilization of several pseudo-components [1–8], here a pseudo-component respresents a group of reactive species that exhibit similar reactivity properties [2]. In air atmosphere, the combustion of lignocellulosic material mainly consists of two sequential phases [9–11]. The first one is the volatilization by pyrolysis, and the second is the oxidation of the resulting char. The two phases should be jointly considered for developing kinetic models of the combustion of lignocellulosic material.

So far, there have been numerous reports on the modeling of pyrolysis and combustion of lignocellulosic materials. Many works studied pyrolysis [1,4,5,12–14] or combustion [11,15,16] of a specific lignocellulosic material independently, which resulted in distinct models of pyrolysis and combustion. For example, for pyrolysis of wheat straw, Lanzetta and Di Blasi [17] suggested a two-step consecutive reaction model, while Mani et al. [18] suggested a model with three parallel nth-order reactions. For the NaCl-treated cellulose, Varhegyi and Antal [19] suggested that both independent parallel reactions and successive reactions can be used to describe the pyrolysis kinetics with identical kinetic parameters. Also distinct kinetic schemes were often used in combined kinetic analysis of pyrolysis and combustion processes. For example, Chen et al. [10] used a scheme consisting of three independent parallel reactions to model the pyrolysis of forest peat, and at the same time, they adopted a two-step consecutive reaction scheme to model the peat combustion. Barneto et al. [20] presented a joint study on the pyrolysis and combustion of biomass, in which they used three nth-order parallel reactions (representative of the thermal degradation of cellulose, hemicellulose and lignin) to describe the biomass pyrolysis, while in the combustion model, they assumed that biomass is only composed of two pseudo-components which represent holocellulose and lignin, respectively. In addition, for holocellulose two consecutive reactions were assumed, while for lignin, two competitive reactions were used. For pine needles, based on the shapes of the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves at different heating rates, Font et al. [21] suggested to use four unified parallel reaction steps to model the major pyrolytic reactions in pyrolysis and combustion, while for the 3rd and 4th reactions, they further used two other reactions to model the combustion of char, and two additional reactions for simulation of oxidative pyrolysis.

Besides dehydration, pyrolysis is the first phase of the combustion process. Therefore it is reasonable to develop unified kinetic models for pyrolysis and combustion of lignocellulosic materials. Here the term "unified" means that consistent pseudo-components are considered for the kinetic models of pyrolysis and combustion. Such an effort was made by Conesa and Domene [22]. They used three nth-order parallel reactions to describe both the pyrolysis and combustion of biomass, and the minor difference between them is that a different pre-exponential factor was considered in simulating biomass combustion due to the presence of oxygen. Although with minor local deviation, the experimental and calculated curves for all the five species showed good agreement as a whole (with the global deviation below 5.5%).

The three-parallel-reaction model and the four-parallel-reaction model have been used independently for pyrolysis [4,5] and combustion [11,15]. In this work, we make an effort to establish a unified kinetic description for the major pyrolytic reactions in pyrolysis and combustion of lignocellulosic material, using pine branch as the sample. In the newly proposed kinetic scheme, we first simulate the pyrolysis of the sample by the traditional three-parallel-reaction model, thereby the fractions of cellulose, hemicellulose, and lignin are obtained, which are then used to simulate the combustion process by the four-parallel-reaction model. The forth reaction in combustion is approximated as due to the oxidation of fixed carbon generated from the non-volatilizable component in the original material. The proposed kinetic model is justified by good agreement between the experimental and simulated DTG curves.

2. Experimental

2.1. Materials

The samples used in this study were pine branches (PB, *Pinus sylvestris*) collected from Great Khingan in northeast of China. The samples were collected from living trees to prevent from being polluted or mixed with impurities. Before tests, the samples were kept in a blast-type electric oven for 48 h, with a constant temperature of 85 °C. A mill was used for grinding of samples, and then, sieves were used to classify the sample particles into different groups with different dimensions. The sizes of all the sample particles were in the range of 75–100 μm, for which the conversion is considered to be unaffected by heat and mass transfer effects. Ultimate analysis and proximate analysis were conducted respectively using a Vario EL cube apparatus and the method proposed by Mayoral [23], and the determined material properties are shown in Table 1.

2.2. Thermal analysis experiments

A Netzsch thermobalance model STA 449F3 was used for thermogravimetric (TG) tests. The samples were evenly distributed over the sample pan with the initial mass of 10 ± 0.5 mg. Dynamic experiments were carried out at heating rates of 10, 15 and 20 °C/min, from room temperature up to 700 °C. Nitrogen and air were used as the sweeping gas respectively for pyrolysis and combustion experiments, and the gas flow rate was 50 ml/min. Some runs were repeated to verify the repeatability of the tests under the same conditions.

3. Pyrolysis: results and discussion

3.1. Experimental results

Fig. 1(a) presents the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for pine branch pyrolysis in nitrogen, which show similar variations of mass losses at different heating rates. The first mass loss stage between 27 °C and 150 °C is due to sample dehydration [10,24], which accounts for about 7% of the total mass loss for different heating rates. Pyrolysis mainly occurs within 150–500 °C, and each DTG curve is characterized by a shoulder due to the decomposition of hemicellulose at lower temperatures, a peak mainly attributable to the decomposition of cellulose, and a broad lignin-related tail at higher temperatures [5,18,22,25]. The residues mainly include non-volatilizable fixed