



Comparative pyrolysis behaviors and reaction mechanisms of hardwood and softwood



Yanming Ding^{a,b}, Ofodike A. Ezekoye^b, Shouxiang Lu^{a,*}, Changjian Wang^{c,*}, Ru Zhou^{b,d}

^aState Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230027, China

^bDepartment of Mechanical Engineering, University of Texas at Austin, Austin, TX 78712, USA

^cSchool of Civil Engineering, Hefei University of Technology, Hefei 230009, China

^dJiangsu Key Laboratory of Urban and Industrial Safety, College of Safety Science and Engineering, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Article history:

Received 19 September 2016

Received in revised form 23 October 2016

Accepted 7 November 2016

Keywords:

Wood biomass

Pyrolysis

Thermogravimetry

Kinetics

Mechanism

ABSTRACT

Comparative pyrolysis behaviors of typical hardwood (*Fagus sylvatica*) and softwood (*Cunninghamia lanceolata*) were investigated based on thermogravimetric analysis over a wide heating rate range from 5 K/min to 60 K/min. The Flynn-Wall-Ozawa model-free method was applied to estimate the various activation energy values at different conversion rates, and the Coats-Redfern model-fitting method was used to predict the possible reaction mechanism. Two pyrolysis regions were established by the trend of activation energy, divided by the threshold of conversion rate (0.4 for hardwood and 0.2 for softwood) but with the same distinguished temperature at about 580 K. For the region under the conversion rate threshold, the activation energy of hardwood increased gradually while softwood decreased. Furthermore, the activation energy remained the same for both hardwood and softwood in the region over the conversion rate threshold. However, softwood behaved greater activation energy than hardwood during the whole pyrolysis process. The pyrolysis differences of hardwood and softwood could be attributed to the chemical component, molecular structure, component proportion and various extractives. The same reaction mechanism of hardwood and softwood was verified by applying the Coats-Redfern approach. By checking activation energies obtained according to different models with those obtained through the Flynn-Wall-Ozawa method, the best model was based on diffusion mechanism when the conversion rate was less than its threshold, otherwise based on reaction order (2nd to 3rd).

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Renewable energy production can help countries meet their sustainable development targets and climatic change problems [1], leading researchers to investigate the possibility of using various strains of micro- and macroalgae as feedstocks for renewable fuels [2]. Solid biomass has become one of the most important renewable sources for power and heat generation [3]. Amirante and Tamburrano [4] had demonstrated that the use of small combined cycles for simultaneous generation of heat and power from the external combustion of solid biomass and low quality biofuels was feasible. Wood, as a typically renewable solid biomass, is expected to play a more important role in the energy mix of the future [5]. Suteu et al. [6] proved that the use of wood waste as a renewable energy source, replacing fossil fuels, was technically feasible and economically attractive. Nukman and Sipahutar [7]

also assessed the potential of biomass from wood, leaves, and grass as a source of renewable energy in Indonesia.

Pyrolysis, as one of the promising technology for biomass utilization [8], is the first step of all thermochemical processes occurring in an inert atmosphere [9] based on a series of complex reactions which are influenced by many factors, such as heating rate, temperature and composition of biomass material. The pyrolysis of wood depends on degradation of its three main constituents (hemicellulose, cellulose, and lignin) [10]. Cellulose is highly crystalline, but hemicelluloses and lignin are amorphous [11]. These three compounds show different thermal degradation behaviors because of different chemical compositions and structures: hemicellulose, which is composed of heteropolysaccharide including amorphous and branched structure, decomposes first at low temperatures, while cellulose exhibits a more thermal resistance with a sharper degradation range, and lignin decomposition happens in a very broad range but with a reduced volatilization compared with the other two compounds [3].

* Corresponding authors.

E-mail addresses: sxlu@ustc.edu.cn (S. Lu), chjwang@ustc.edu.cn (C. Wang).

Wood biomass is grouped into two large groups: hardwood and softwood [12]. For a better understanding of the pyrolysis process difference between hardwood and softwood, many researchers studied their thermal decomposition process. Gronli et al. [13] compared the thermogravimetric curves of several hardwoods and softwoods and showed that the decomposition of softwood started at lower temperatures and the hemicellulose and cellulose zone were wider than that of hardwood. Meanwhile, a model-fitting method was applied to estimate the activation energy of hemicellulose, cellulose and lignin. García-Pérez et al. [14] conducted the vacuum pyrolysis experiment and compared the product yields and bio-oil properties of hardwood and softwood, but without estimating the activation energy. The pyrolysis mechanisms of O-acetyl-preserved hemicelluloses isolated from both hardwoods and softwoods was investigated by Wang et al. [15] and showed that hardwood hemicellulose pyrolysis had lower activation energies than softwood hemicellulose pyrolysis by the distributed activation energy model coupled with the double-Gaussian functions model-fitting method. Moreover, Liu et al. [16] focused on the mechanism study of hardwood (birch wood) and softwood (fir wood) lignin pyrolysis by thermogravimetric analysis coupled with Fourier transform infrared spectrometry analysis, and the estimated activation energy of lignin was in the range of 72.9 kJ/mol and 141.7 kJ/mol with the Coats-Redfern model-fitting method, whereby the activation energy of softwood lignin was lower compared with that of hardwood lignin. Furthermore, the average activation energy of hardwood (maple wood) and softwood (pine wood) during the pyrolysis process was estimated by Yao et al. [17] based on multiple model-free methods, about 150 kJ/mol for hardwood and 160 kJ/mol for softwood.

However, there are not many studies comparing the pyrolysis of hardwood and softwood based on the model-free coupled with model-fitting method, especially the activation energy trend and pyrolysis reaction mechanisms. As usual, the reaction order model is assumed as the appropriate reaction mechanism of wood biomass, but it should be confirmed its feasibility during the whole pyrolysis process. In order to fill the gaps in knowledge, thermogravimetric analysis, as a high-precision and common method [1] used for kinetic analysis of devolatilization process, is applied in this paper. Our study focuses on thermogravimetric curves of typical hardwood and softwood on various heating rates, the estimation of chemical kinetic parameters by the Flynn-Wall-Ozawa model-free method and the prediction of reaction mechanism by the Coats-Redfern model-fitting method, as well as their differences throughout the thermal degradation process.

2. Materials and methods

2.1. Sample preparation

Beech wood (*Fagus sylvatica*) used before [18] is considered as the typical hardwood, which is native to temperate Europe, appropriate for furniture, tools and small household articles [19]. Chinese fir (*Cunninghamia lanceolata*), as one of the important native softwoods, widely planted in mountainous areas in the tropics and subtropics in China for more than one thousand years [20], is chosen as the typical softwood. The elemental analysis was conducted by an elemental Vario EL cube, and the measured results were listed in Table 1. The wood samples were milled to less than 0.2 mm in advance [21], avoiding the temperature gradient within the particles during the next thermogravimetric measurements.

2.2. Thermogravimetric measurements

The thermogravimetric experiment involved drying of both samples at 80 °C for about 24 h prior to pyrolysis, removing the

Table 1

Elemental and chemical analysis of wood sample (% mass, dry basis).

| Elemental and chemical analysis | <i>F. sylvatica</i> ^b | <i>C. lanceolata</i> ^c |
|---------------------------------|----------------------------------|-----------------------------------|
| C | 45.52 | 48.13 |
| H | 6.34 | 6.46 |
| N | 0.16 | 0.13 |
| O ^a | 47.98 | 45.28 |
| Hemicellulose | 28.3 | 11.9 |
| Cellulose | 41.2 | 48.9 |
| Lignin | 22.2 | 31.2 |
| Ash | 0.48 | 0.25 |

^a Oxygen content was obtained by difference.

^b Information from Ding et al. [18] and Telmo et al. [22].

^c Chemical information from Liu et al. [16].

free water. A TA Instrument SDT Q600 thermal analyzer was applied in the pyrolysis process from 300 K to 1000 K. The sample weight was approximately 6 mg and evenly placed in an Alumina cup without a lid. The high purity nitrogen (100 mL/min) was used as a purge gas to sweep the produced gas away from the sample. Four heating rates were employed for hardwood and softwood sample pyrolysis: 5, 10, 20 and 60 K/min.

2.3. Pyrolysis kinetics

Kinetic equation for pyrolysis of solid state can be expressed based on conversion rate as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the conversion rate during pyrolysis, $k(T)$ is the reaction rate constant which can be explained by the Arrhenius law and $f(\alpha)$ is the function of reaction mechanism. Whereby, α and $k(T)$ can be calculated with Eqs. (2) and (3), respectively.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where m_0 , m_t and m_∞ refer to the sample mass at the initial time, time t and the end, respectively. A is the pre-exponential factor and E_a is the activation energy of the reaction. R is the universal gas constant, and T is the reaction absolute temperature.

Considering a linear heating rate, $\beta = dT/dt$, Eq. (1) can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

The integration function of conversion is expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (5)$$

where T_0 is the initial absolute temperature. This integral expression is the fundamental equation that preambles the determination of non-isothermal solid thermal degradation kinetic methods to determine the kinetic mechanisms parameters [23].

Two common isoconversional methods are applied in the paper: the Flynn-Wall-Ozawa (FWO) and Coats-Redfern (CR) methods. FWO is a model-free method [24] which was developed by Flynn and Wall [25], as well as Ozawa [26]. The method requires the measurement of the temperatures corresponding to fixed conversion rates from experiments at different heating rates [27], and then obtains the activation energy (E_a) of a solid state reaction without prior knowledge of the reaction mechanisms [24]. CR is a model-fitting method [24] which was developed by Coats and

Download English Version:

<https://daneshyari.com/en/article/5013082>

Download Persian Version:

<https://daneshyari.com/article/5013082>

[Daneshyari.com](https://daneshyari.com)