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Thermal decomposition kinetic of hybrid poplar sawdust as biomass to biofuel

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ABSTRACT

In order to reveal the kinetic mechanism of thermal decomposition of hybrid poplar sawdust as biomass to produce biofuel, the thermogravimetric experiments were carried out at four different heating rates, 5, 10, 15 and 20 °C min^{-1} using a thermogravimetric analyzer under air atmosphere. The kinetic analysis was performed according to the Ozawa-Flynn-Wall method. The results showed that the activation energy altered from 38.08 kJ/mol to 141.47 kJ/mol. The pre-exponential factor values showed empirical first order reaction. The Gibbs free energy values changed from 102.76 kJ/mol to 184.82 kJ/mol, and the entropy changes were negative, showing that the disorder degree of products obtained by degradation was lower than that of initial compounds. The calorific value of the biomass was 19539 kJ/kg.

1. Introduction

The biofuel can be generated from a variety of biomass, including wastes from agriculture, municipal solids, industry, and forestry. Forestry wastes are a kind of plentiful materials with high cellulose content. Statistics data show 37 million cubic meter of forestry wastes are generated every year in China [1]. Hybrid poplar with fast-growing, low-cost and fine tissue is widely used in furniture and building industry [2]. Thus, the hybrid poplar sawdust from wood processing is enormous [3]. It is of great value to use the hybrid poplar sawdust for biofuel production. However, the reuse and thermochemical properties of hybrid poplar sawdust have not been studied.

The quantity and quality of the recovered bioenergy depend not only on the process conditions but also on the chemical composition of raw materials. Research has demonstrated that the presence of cross-link between hemicellulose and cellulose with lignin via ether and ester linkages could cause the biomass recalcitrance [4]. Thermochemical degradation kinetics could exactly reflect the recalcitrance degree and feasibility of the thermochemical conversion into biofuels. Thus, it is important to comprehend the thermochemical degradation kinetics of the biomass in order to reveal the process mechanism of the thermochemical conversion into biofuels.

This study investigated thermochemical degradation kinetics of hybrid poplar sawdust including thermodynamic parameters for non-isothermal analyses by Ozawa-Flynn-Wall model, and the values of pre-exponential factor (A), apparent activation energy (*Ea*) in Arrhenius equation, and then the changes of free Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated. Finally, the calorific value was obtained using calorimetric bomb.

2. Materials and methods

2.1. Materials

Hybrid poplar sawdust was collected from Yulin furniture factory, Shannxi, China and chemical constituents of the hybrid poplar sawdust are showed in Table 1. The sawdust was rinsed in distilled water and air-dried for 2 days, and dried at 105 °C to constant weight, and then the sawdust was ground and sieved (80 mesh, 0.178 mm). The obtained sample was sealed in glass bottle and stored at room temperature.

2.2. Thermal analysis and calorific value

Thermogravimetric analysis were performed at four different heating rates, 5, 10, 15 and 20 °C min^{-1} by a TGA-DTG-DSC analysis equipment (SDT Q600), and test range was 25–1000 °C under 120 ml min^{-1} air flow rate. In each analysis, 2 mg sample was used in Al_2O_3 crucible. Calorific value analysis was carried out using a

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Table 1
Chemical composition of the hybrid poplar sawdust.

Constituent	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Volatile (%)	Fixed carbon (%)
Content (%)	45.10	17.91	26.12	1.69	86.33	16.56

Calorimetric Bomb (SHR-15), and 1 g sample was used for 10 min with pure oxygen (purity > 99.2%).

2.3. Kinetics analysis

The degradation processes is considered as a single reaction [5].

$$Biomass \xrightarrow{k} Volatiles + Biochar \quad (1)$$

k is the rate constant of degradation reaction and is defined as below [6]:

$$k = Aexp(-Ea/RT) \quad (2)$$

Where A is the pre-exponential factor, s^{-1}; Ea is apparent activation energy, kJ/mol; R is universal gas constant, 8.314 J/K mol^{-1}; T is the absolute temperature, K.

The conversion rate is described by Eq. (3).

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3)$$

Where α is conversion degree ($\alpha = \frac{m_0 - m}{m_0 - m_\infty} \times 100\%$); t is the time of process; m_0 is the initial mass of the sample; m is the mass at time t; m_∞ is the mass after combustion [7].

For single reaction, $f(\alpha)$ is defined as below [5]:

$$f(\alpha) = (1-\alpha)^n \quad (4)$$

Where n is the order reaction.

Combining Eqs. (2), (3), (4) and heating rate $\beta = dT/dt$ gives the expression (5) to compute kinetic parameters according to TG results.

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{Ea}{RT}\right)(1-\alpha)^n \quad (5)$$

In this study, the activation energy can be gained by TG/DTG. The thermodynamic parameters are calculated by Ozawa-Flynn-Wall model at different heating rates.

Kinetic parameters are important to infer the reactions behavior and to optimize the reactions process [7]. The Ozawa-Flynn-Wall model Eq. (6) is used [8].

$$ln\beta = C_\alpha - \frac{E_a}{RT} \quad (6)$$

Where β is heating rate; $C\alpha$ is function of α.

The Ozawa-Flynn-Wall model is applied at least three heating rate values for same and different conversion degree values obtained by thermogravimetric curves. In order to obtain the kinetic parameters, the used β was 10 °C min^{-1} in this work.

The kinetic parameters using Ozawa-Flynn-Wall model for kinetics analysis and kinetic parameters including pre-exponential factor, and the changes of Gibbs free energy, enthalpy, and entropy can be described using Eqs. (7)–(10) [7,8].

$$A = \beta \cdot E_a \exp\left(\frac{E_a}{RT_p}\right)/RT_p^2 \quad (7)$$

$$\Delta G = E_a + RT_p \cdot \ln\left(\frac{K_B \cdot T_p}{h \cdot A}\right) \quad (8)$$

$$\Delta H = E_\alpha - RT \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (10)$$

Where K_B is Boltzmann constant, 1.381×10^{-23} J/K; h is Plank constant, 6.626×10^{-34} Js; T_p is peak temperature of DTG.

3. Results and discussion

3.1. Thermogravimetric analysis

Thermal degradation of lignocellulosic biomass can be divided into individual stages: devolatilisation of water, and decomposition of hemicellulose, cellulose and lignin [9]. The degradation process consists of combustion, pyrolysis, and oxidative pyrolysis [10]. From 180 °C to 900 °C, lignin thermal degradation occurs, and decomposition of hemicellulose and cellulose occurs in the temperature range from 220 °C to 315 °C and from 315 °C to 400 °C, respectively. Maximum mass loss rate is about 268 °C and 355 °C [11].

The TG/DTG curves indicate the changes of physicochemical structural during the thermal degradation process. DTG curve shows main devolatilisation steps more obviously [12].

The thermal degradation temperature up to 1000 °C with the heating rate of 5, 10, 15 and 20 °C min^{-1}, 94.77%, 94.99%, 97.98% and 93.36% of the biomass were volatilized, with a 5.23%, 5.00%, 2.01% and 6.63% of residues, respectively. The biochar formed in the temperature range from 260 °C to 490 °C. The presence of oxygen can induce fractional oxygenation of solid, leading to the delay of biomass decomposition.

Fig. 1 showed TG and DTG curves of hybrid poplar sawdust at different heating rates. The experimental data indicated that the thermal degradation process of the biomass was complicated. The thermal decomposition of hydrocarbons and volatiles ingredients at the hybrid poplar sawdust it was at about 260 °Cas can be seen from Fig. 1 (stage 1) [13]. This step it was went with thermal degradation what implied that the biomass possessed thermal stability [14,15], and then followed by the devolatilisation step which was a main mass loss in a range from approximately 260 °C to 470 °C releasing the volatiles organics (stage 2) [16,17]. In stage 2, intermolecular and intramolecular hydroxy broke off and formed into water. Carbonyl was formed. Glycosidic bond, cyclic C—O bond and C—C bond ruptured and formed into a series of tar substances (such as acids, alcohols, aldehydes, ethers) and gas compounds such as CO, CO_2 and CH_4 [18]. After devolatilisation step, dealkylation and aromatization condensation reaction were continued, and some carbohydrates such as cellulose began to degrade, and thermal decomposition of lignin followed closely with the temperature increasing. The lignin decomposition started at the below temperatures and above 550 °C [19] (stage 3). In this stage, the final products such as CO, CO_2 and CH_4 were formed [20,21]. The region of high temperature was the thermal stability, and the region of high temperature occurred oxide formation (stage 4) [7,22].

The relationship of biomass and the lignin, hemicellulose and cellulose fractions was not precise [7]. However, the different