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Thermogravimetric study and kinetic analysis of fungal pretreated corn stover using the distributed activation energy model

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HIGHLIGHTS

- ▶ Fungal pretreatment can accelerate thermal degradation and slightly affect the shapes of TG and DTG curves.
- ▶ The temperature corresponding to maximum weight loss rate shows a lateral shift to higher temperature with the heating rate.
- ▶ The activation energies of coculture-pretreated corn stover were lower than that of monoculture pretreated.

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ABSTRACT

Non-isothermal thermogravimetry/derivative thermogravimetry (TG/DTG) measurements are used to determine pyrolytic characteristics and kinetics of lignocellulose. TG/DTG experiments at different heating rates with corn stover pretreated with monocultures of *Irpex lacteus* CD2 and *Auricularia polytricha* AP and their cocultures were conducted. Heating rates had little effect on the pyrolysis process, but the peak of weight loss rate in the DTG curves shifted towards higher temperature with heating rate. The maximum weight loss of biopretreated samples was 1.25-fold higher than that of the control at the three heating rates, and the maximum weight loss rate of the co-culture pretreated samples was intermediate between that of the two mono-cultures. The activation energies of the co-culture pretreated samples were 16–72 kJ mol^{-1} lower than that of the mono-culture at the conversion rate range from 10% to 60%. This suggests that co-culture pretreatment can decrease activation energy and accelerate pyrolysis reaction thus reducing energy consumption.

1. Introduction

Agricultural residues are promising energy feedstocks for biofuel productions via biochemical or thermochemical conversion (Demirbas and Balat, 2006). Thermochemical conversion includes combustion, liquefaction, pyrolysis, and gasification (Cantrell et al., 2008). Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel at high temperature in the absence of an oxidizing agent (air/oxygen). With the addition of heat and catalysts, the biomass breaks down to condensable vapors, non-condensable gasses (pyrolysis gas), and charcoal. All products are combustible. The condensable vapors form a liquid known as bio-oil, pyrolysis oil or crude oil, which contains a large number of oxygenated organic compounds with a wide range of molecular weights and a small amount (<1%) (Diebold, 2002; Demirbas, 2009).

Thermogravimetric analysis (TGA) is one of the commonly used techniques to study thermal events during pyrolysis of biomass and other fuels (Aboulkas and El Harfi, 2009). TGA is usually used as a means of determining pyrolytic characteristics and kinetic parameters (Williams and Ahmad, 2000; Zhao et al., 2010). TGA measures the amount and rate of change in the weight of a tested material as a function of temperature or time in a controlled atmosphere, such as nitrogen atmosphere or air. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000 °C. The technique can characterize materials that exhibit weight loss or gain during the heating process due to: decomposition, oxidation, or dehydration. The various weight loss processes determined during the TGA reflect the physical and chemical structural changes during the conversion. Differential thermogravimetry (DTG) curve highlights the various TG processes more clearly (Huang et al., 1996). Kinetic analyses have become a crucial point in thermal analysis, in which the main purpose is to determine the mechanism(s) of decomposition and to calculate the parameters of the Arrhenius equation (Noisong et al., 2009). Numerous kinetic

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models have been used for the analysis of thermal decomposition processes. These models can be grouped in single-reaction and multi-reaction models. The Coats–Redfern model (Coats and Redfern, 1964) considers pyrolysis as single and independent first order parallel reactions and is widely used to determine the kinetic parameters of thermal decomposition (Tsamba et al., 2006). The model assumes that there is no interaction between hemicellulose, cellulose, and lignin in biomass. However, Worasuwannarak et al. (2007) proved that there were significant interactions between cellulose and lignin during pyrolysis. Additionally, inorganic materials influence pyrolysis pathways (Jensen and Johansen, 1998). A simplified model, known as distributed activation energy model (DAEM) has been proposed by Miura (1998) and has been widely used to analyze such complex reactions. The model assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously.

Non-isothermal TGA/DTGA has been widely used to determine the kinetic parameters of biomass and other materials, such as polypropylene. Compared with conventional isothermal experiments, non-isothermal experiments are more convenient to carry out because it is not necessary to increase the temperature suddenly at the beginning. Moreover, non-isothermal kinetics requires fewer data for evaluating and analyzing the kinetic parameters (Maitra et al., 2008; Choudhury et al., 2007).

Corn stover can be converted to bio-oil through thermochemical conversion, but this bio-oil is not suitable as a vehicle fuel because of its high oxygen content, high acidity and instability (Lu et al., 2009). Pretreatment is an effective way to upgrade its quality and improve the efficiency of the pyrolysis process (Hassan et al., 2009; Misson et al., 2009; Eom et al., 2011). Recent studies showed that biological pretreatment with white rot fungi can accelerate thermal degradation and alter the composition of the pyrolysis products (Yang et al., 2010, 2011; Ma et al., 2011). Different white rot fungi with different degradation patterns and their co-culture may have different effects on pyrolytic characteristics and pyrolysis products (Ma et al., 2011). The effects of different pretreatment methods on pyrolytic characteristics are summarized in Table 1.

The objective of this study was to investigate the thermal behavior of corn stover treated with fungal mono- and co-cultures and to determine the influence of the heating rate on the thermal behavior of these samples. Also, the kinetic parameters for thermal decomposition of these samples were calculated using the DAEM method, and the results are compared with that of Coats–Redfern method.

2. Methods

2.1. Fungal strains

Irpex lacteus CD2 was isolated from the Shennongjia Nature Reserve (Hubei, China) and can degrade lignin (Xu et al., 2009). *Auricularia polytricha* AP was obtained from the Culture Collection Center, Huazhong Agricultural University (Hubei, China). The two fungi are white rot fungi and can grow well on corn stover substrate. They can be co-cultivated in liquid and solid substrates. The fungi were maintained on potato dextrose agar (PDA) slants at 4 °C and cultured on PDA slants for one week before use. The fungi were inoculated into the center of 9 cm PDA plates and grown at 28 °C for one week. Five disks cut from the margin of active fungal cultures on PDA plates were inoculated into a 250 ml Erlenmeyer flask with 100 ml of potato dextrose broth (PDB) pH 5.5 and incubated at 28 °C, 150 r/min for 5–7 days. The mycelia washed with sterile distilled water, transferred to a sterile Waring blender cup containing 100 ml of sterile distilled water, and homogenized were used as inoculums for biological pretreatment of corn stover.

2.2. Biological pretreatment of corn stover

Corn stover from Enshi City (Hubei, Province) was milled to pass through an 80-mesh screen. Several 250 ml Erlenmeyer flasks containing 10 g of corn stover and 25 ml distilled water were autoclaved for 30 min at 121 °C, cooled and 10 ml inoculums of *A. polytricha* AP, or *I. lacteus* CD2, or a mixture of both organisms (8 ml of *A. polytricha* AP and 2 ml of *I. lacteus* CD2), respectively were added. All flasks were incubated statically at 28 °C for 15 days. Non-pretreated corn stover was sterilized by autoclaving and used as a control.

2.3. Thermogravimetric analysis

After pretreatment, the samples were dried at 60 °C for 3 days and ground with Philips mixer grinder to a particle size <0.18 mm. Thermogravimetric experiments were performed using a highly accurate thermobalance (PerkinElmer, Diamond) at the Analytical and Testing Center, Huazhong University of Science and Technology, at heating rates of 10, 20 and 30 °C/min up to a final temperature of 1000 °C under a nitrogen flow rate of 30 ml/min.

2.4. Analysis of kinetic parameters

The DAEM and Coats and Redfern methods were employed to calculate the activation energy (E), which is one of Arrhenius parameters

The DAEM method assumes that all the reaction activation energies have the same k_0 at the same conversion rate and that the activation energy has a continuous distribution. The DAEM is represented as follows when it is applied to represent the change in total volatiles (Miura, 1998):

$$1 - V/V^* = \int_0^\infty \exp\left(-\frac{k_0}{a}\int_0^T e^{-E/(RT)}\,dT\right)f(E)\,dE \tag{1}$$

where V is the volatile content at temperature T, V^* is the effective volatile content, k_0 is the frequency factor corresponding to the E value, $f(E)$ is a distribution curve of the activation energy that represents the difference in the activation energies of the many first-order irreversible reactions. The distribution curve $f(E)$ is normalized to satisfy

$$\int_0^\infty f(E)\,dE = 1 \tag{2}$$

The distribution function value has an important role in determining the contribution rate of the total volatiles released. Eq. (1) can be simplified to Eq. (3)

$$V/V^* = 1 - \int_{E_s}^\infty f(E)\,dE = \int_0^{E_s} f(E)\,dE \tag{3}$$

where E_s is the activation energy at a given temperature. The $f(E)$ is the normalized distribution curve of the activation energy of many reactions. The Arrhenius equation can be described as follows (Miura, 1998):

$$\ln\left(\frac{a}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) + 0.6075 - \frac{E}{R}\frac{1}{T} \tag{4}$$

Using Eq. (4), both activation energy and frequency factor can be determined from the slope and intercept of the Arrhenius plot.

Coats and Redfern method (1964) has been widely applied to study the thermal decomposition kinetics of biomass. The reaction kinetic equation is:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{5}$$