International Biodeterioration & Biodegradation 65 (2011) 410–414

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Thermal decomposition kinetics of wheat straw treated by *Phanerochaete chrysosporium*

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ARTICLE INFO

Article history:
Received 4 September 2010
Received in revised form
14 December 2010
Accepted 15 January 2011
Available online 17 February 2011

Keywords:
Biological pretreatment
White-rot fungus
Wheat straw
Pyrolysis
Thermal degradation

ABSTRACT

Combining biological pretreatment with thermal processing may offer an alternative strategy for efficient conversion of lignocellulosic biomass into fuels and chemicals. The thermal decomposition kinetics of biologically pretreated wheat straw by *Phanerochaete chrysosporium* was investigated in this study using thermogravimetry (TG) – deconvoluted thermogravimetry (DTG) techniques and the Friedman method. This study revealed that biological pretreatment reduced the thermal degradation temperature of the biomass significantly. Relying on the thermal behavior of the biologically pretreated wheat straw, we proposed two biomass degradation phases during the biological degradation of wheat straw. The first phase of biodegradation (within 10 days of biological pretreatment) improved the efficiency of pyrolysis by reducing the temperature demand. In the second phase (after 10 days), although the efficiency of pyrolysis displayed the similar trend as the first phase, it showed a significant increase in activation energy demand. This process is greatly influenced by the residual lignin and cellulose ratios in the biomass. These experimental results will be useful in developing a biological pretreatment based thermochemical conversion process for lignocellulosic biomass.

1. Introduction

The conversion of lignocellulosic biomass to biofuels possesses great potential for the production of bioenergy. Among the various lignocellulosic biomass conversion technologies, pyrolysis is one of the popular technologies, which is characterized by thermal conversion of biomass into fuels and chemicals in the absence or significantly small amounts of oxygen (Mohan et al. 2006). In general, as a simple and fast technology, pyrolysis processes a wide variety of feedstocks and potentially uses all of the products to converting high-value products. However, the poor selectivity in terms of product formation during pyrolysis is considered a drawback to the commercialization of the process (Kawamoto and Saka 2007). Biomass pretreatment prior to the thermal application may offer a solution for improving the selectivity of the pyrolysis process because pretreatment results in the partial breakdown of bridges among the lignocellulosic major structures: lignin, cellulose, and hemicellulose. Previous studies on the pyrolysis of chemically pretreated biomass helped to improve the pyrolytic products yield (Dobele et al. 2003; Das et al. 2004; Johnson et al. 2009). However, there are very few reports on microbe-pretreated biomass followed by thermal degradation. Among the microorganisms that are capable of degrading lignocelluloses, white rot fungi has a higher selectivity towards lignin and does so with lower energy input, as well as being environmentally benign (Singh and Chen 2008). Degradation of lignin by white rot fungi facilitates its access to holocellulose, which is its actual carbon and energy source while degrading the plant cell wall (Chen et al. 2010). This depolymerization and deconstruction process will relax the structure of the biomass and change the lignocellulosic compositions. If this partial biodegradation process is combined with the thermal degradation process, it may (1) increase the selective production of lignin derived or cellulose derived compounds, (2) diminish the thermal decomposition temperature, (3) increase the thermal conversion rate, and (4) reduce the required thermal decomposition energy. Therefore, combining biological pretreatment with pyrolysis may be a promising methodology for the efficient conversion of biomass into biofuels and chemicals.

In general, before implementing the pyrolysis process, the thermal behavior of the biomass should be verified. Thermogravimetry analysis (TGA) has been proven as a useful tool to analyze the thermal behavior of biomass (Lu et al. 2009). It provides information about the pyrolysis decomposition profile of the biomass and associated reaction kinetics. It is also frequently

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doi:10.1016/j.ibiod.2011.01.004

employed in the kinetic modeling of thermal degradation of biomass-type wastes (Varhegyi et al. 1997; Li et al. 2008). The rate of release, quantity, and composition of the volatiles influence flame ignition, stability, and the temperature profile in the radiant section of the furnace, which is dependent on the heating rate, pressure, particle size, temperature, and the presence of ash or mineral deposits in the substrates (Fisher et al. 2002). Yang and colleagues (2010) demonstrated lower energy demand for biologically pretreated corn stover during TGA. Similarly, in another study, the soft-rot fungus *Trichoderma viridae* was able to increase the temperatures of water desorption and the cellulose decomposition process and lower the thermal stability of lime wood (Popescu et al. 2010). Recently, we have also found that pretreating wheat straw with *Phanerochaete chrysosporium* tends to decrease the crystallinity of cellulose, resulting in significant sugar release during the enzymatic hydrolysis of those samples and also leads to product distribution changes during pyrolysis GC-MS (Zeng et al. 2011).

The current work demonstrates the thermal decomposition process of *P. chrysosporium* grown on spent wheat straw. We employed the Friedman equation to calculate the kinetic parameters as described previously (Lu et al. 2009; Ren et al. 2009), and investigated how biological pretreatment affects the biomass structure, as well as how these changes lead to differences in thermal degradation patterns. By exploring the thermal degradation kinetics of biologically pretreated wheat straw, this study will be useful for developing biological pretreatment based thermochemical conversion methodologies for converting biomass into biofuels and chemicals.

2. Materials and methods

2.1. Overview of the experiment

We used wheat straw as a lignocellulosic biomass and *P. chrysosporium* as the biocatalyst producer. The fungus was grown in wheat straw at 37 °C for ten and twenty days. The biologically pretreated wheat straw was subjected to grinding with a hammer mill and the dried biomass was used for chemical composition analysis. To determine the thermal degradation behavior of biologically pretreated wheat straw, TG/DTG analyses were applied at different heating rates and Friedman analysis was used to evaluate the kinetic values.

2.2. P. chrysosporium cultivation and biological pretreatment

Two groups of 20 g wheat straw (*Triticum sativum*, grown in Moscow, Idaho) were autoclaved with water before inoculation with 100 ml of *P. chrysosporium* ATCC 24725 spores. The cultures were incubated at 37 °C for ten and twenty days.

2.3. Chemical compositional analysis of the biomass

The chemical compositional analysis of the biomass was done to determine total lignin and monosugar content of the biomass. For this, the dry straw was ground and sieved through size 60 mesh sieving screens. 0.5 g biomass was extracted with tolune:ethanol as described by ASTM method 1107. Wheat straw samples were prepared and characterized by the two-stage acid hydrolysis method described by Standard Biomass Analytical Procedures (NREL) [TAPPI test method (T22-om 88)]. The sugars in the aqueous phase were quantified by ion chromatography using an ion exchange chromatography column (Dionex ICS-3000 DC IC) equipped with an electrochemical detector. Acid-soluble lignin was determined by UV absorbance at 205 nm with an extinction coefficient of 110 L g^{-1} cm^{-1} (Zimbardi et al. 1999).

2.4. Thermogravimetric analysis

To analyze the degradation of biomass in the slow pyrolysis process, thermogravimetric analysis (TGA) was conducted with the Mettler Star^e system (Mettler Toledo TGA/SDTA 851^e, Switzerland). Weight loss experiments were performed on the fungal spent wheat straw samples weighing 5–6 mg. The selected heating rates were 10 °C min^{-1}, 20 °C min^{-1}, 30 °C min^{-1}, 40 °C min^{-1}, and 50 °C min^{-1} under a nitrogen atmosphere (flow rate of 20 ml min^{-1}). Based on the different heating rates, activation energy needed for biomass degradation was determined by using Friedman equations.

2.5. Mathematical methods used to determine kinetic parameters of pyrolysis

Due to the limitation of using a single heating rate to evaluate the biomass kinetic parameters, (Burnham 2000), the Friedman equation (1) was used under different heating rates β as described in methodology section. The Friedman method is an isothermal analysis method used to calculate activated energy (E) and the pre-exponential factor (A) of the samples.

$$\ln\left(\frac{d\alpha}{dt}\right) = \mathrm{In}f(\alpha) + \ln A - \frac{E}{RT} \quad (1)$$

where $d\alpha/dt$ = instantaneous reaction rate, α is the mass fraction at time t, A is the pre-exponential factor, E is the activated energy, R is the gas constant, and $f(\alpha)$ is the reaction mechanism function.

To determine the three-pseudocomponents, the following model equations were used (Johnson et al. 2009):

$$\frac{d\alpha}{dt} = \sum_{j=1}^{N} Z_{jo}\frac{d\alpha_j}{dt} \quad (2)$$

$$\frac{d\alpha_j}{dt} = A_j \exp\left(-\frac{E_j}{RT}\right)(1-\alpha_j)^n \quad (3)$$

$$\sum_{j=1}^{N} Z_{jo} = 1 \quad (4)$$

$$Z_{jo} = \frac{W_{jo} - W_{j_\infty}}{W_o - W_{j_\infty}} \quad (5)$$

where $d\alpha/dt$ = instantaneous reaction rate, $d\alpha_j/dt$ = instantaneous reaction rate for component j, the α_j = parameter is defined as $\alpha_j = (W_{jo} - W_j)/(W_{jo} - W_{j\infty})$, Z_{jo} = mass fraction of volatile solids from component j, A_j = pre-exponential factor corresponding to thermal degradation of component j, E_j = activation energy corresponding to component j thermal volatilization, and W = mass of solid residue.

3. Results and discussion

3.1. TGA and DTG of biologically pretreated wheat straw

The chemical composition of wheat straw after treatment with *P. chrysosporium* for different time periods is presented in Table 1. The data shows a continuous decrease in acid insoluble lignin and holocellulose content in fungal treated wheat straw. However, the ratio of lignin to glucose rose from 0.7 to 0.9. Fig. 1 shows the TGA