



Effect of pyrolysis conditions on levoglucosan yield from cotton straw and optimization of levoglucosan extraction from bio-oil



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ABSTRACT

Fast pyrolysis of cotton straw was performed under different temperature ranges, particle sizes, holding times and acid concentrations in a fluidized bed reactor to maximize the yield of levoglucosan (LG). The maximum LG yield was obtained at the optimal pyrolytic conditions: temperature of 500 °C, holding time of 1.4 s, particle size of 600–650 μm and acid concentration of 8%. Furthermore, an improved method to quickly and easily extract LG from bio-oil was developed by utilizing precipitation and Soxhlet extraction to quantitatively remove organic colloid, pigments and aromatic compounds with less loss of LG during extraction. The process was optimized by using Box-Behnken design for three reaction parameters: the volume of water (A), the quality of activated carbon (B), and pH (C). The extraction presented required no prolonged high heating (thus protecting the LG from hydrolysis), used benign reagents, and realized a significant purity over other methods. The purity and structure of LG were determined by using chromatographic and spectroscopic techniques, such as HPLC, FT-IR and NMR spectroscopy. The optimal extraction yield of LG from the straw bio-oil was 78% with the purity of 95.56%. This research also applied a new method to quickly determine the quantitative and qualitative analysis test parameters of LG.

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1. Introduction

The studies of degradation and bioconversion of biomass have been given much attention because of the depleting fossil fuel problems [1]. Furthermore, only a small portion of chemicals made by fossil fuel could be degraded [2–4]. It is also widely accepted that carbon emission from burning fossil fuel contributes to the global warming [2]. Therefore, if making full use of biomass, not only can biomass relieve the stress of fossil fuel using, but also can have a way of sustainable development. Cotton straw is a kind of agricultural residues. In 2015, cotton in China is cultivated in the area of 63 286 000 acres [36], from which huge amounts of cotton straw were produced. It is used generally as a fuel in the countryside, the gas, which produced by burning can pollute the environment. On the other hand, cotton straw contains a high amount of organic constituents (cellulose, hemicellulose, lignin and minor amounts of other organics). There are several studies on the conversion of cotton straw to valuable products by various methods [5,6].

To obtain active ingredients from biomass, some forms of treatments, such as pyrolysis, are necessary [3]. The operating con-

ditions of pyrolysis need very short residence time [4]. Previous studies showed that, many researchers used forestry and agricultural residues and municipal solid waste to obtain pyrolytic oil. Li and Zhang obtained pyrolytic oil from pyrolyzing waste newsprint and cottons [7]. Cao and Liu co-pyrolyzed a mixture of rice husk biomass and waste tire to obtain pyrolytic oil [8], while the pyrolytic oil almost had the same calorific value as diesel oil did. Compared with diesel oil, pyrolytic oil may need three times volume under same calorific value, on the other hand, pyrolytic oil is more expensive than diesel oil. Thus, substituting pyrolytic oil for diesel oil had lower value-added at present. While utilizing small molecule compounds, such as acids, alcohols, phenols and saccharides, which were extracted from pyrolytic oil, had higher value-added, it could be a perspective way to use biomass. Among many chemicals contained in the pyrolytic liquid, LG is an important degradation product. LG, the main component of viscous syrup during the pyrolysis, is attractive for using in many fields because of its unique structure, it can be used for the synthesis of pesticides, growth regulators, macrolide antibiotics, etc [9]. Previous studies identified that many strains of bacteria, yeast and fungi can grow by using LG as sole carbon and energy source [10,11]. For instance, *Aspergillus terreus* K26 could convert pure LG into itaconic acid [10]. *Aspergillus niger* CBX 209 produced citric acid from LG [11]. Bennett used LG from pine-derived pyrolysis oil, and recovered in the aqueous phase

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Table 1
Main characteristics of the cotton straw.

Parameter analysis	Value (%)
Cellulose	45.54
Hemicellulose	20.07
Lignin	16.82
Extractive	11.86
Ash	5.71

prior to hydrolysis and fermentation to produce bio-ethanol [12]. In both of these experiments, the rates of fermentation yield from LG to other chemicals were comparable to dextroglucose. These findings showed that with specify microorganism, LG can be fermented effectively, and can be used by particular biocatalysts as carbon and energy source. Many scholars used LG to produce bio-ethanol [11]. Yu and Zhang used cotton pyrolytic oil to extract LG and then removed its toxicity to obtain ethanol. Li and Zhang obtained LG from waste newsprint and cottons pyrolytic oil to hydrolyze to get glucose, and then used glucose to obtain bio-ethanol.

The extraction of LG from bio-oil was demonstrated firstly in 1960s. Crown Zellerbach Company used trichloromethane as decolorant and acetone as solubilizer to obtain LG from waste paper pyrolysis oil. High purity LG was extracted from the pyrolysis oil with a low yield. Furthermore, using too much organic solvents on the extraction of LG cannot avoid having an environmental impact [13]. Midwest Research Institute Company used precipitation, common distillation and extraction to obtain LG from the pyrolysis oil. However, under these treatments, too much organic colloid and pigments still existed in LG which had bad effect on LG extracting [14]. In 1991, Gander obtained LG with high purity (98.8%) from the starch pyrolysis oil with chromatographic separation and rotary evaporation. Though obtained higher purity LG with lower pollution, the starch related to the problem of “competing food with human”, this method was not a promising way [15]. In 2001, Zhang Hongxun used ion exchange chromatography several times to separate LG from cellulose pyrolysis oil. Although this method had a higher yield of LG, it was rather labour intensive and time consuming [16]. Thus, developing methodology for an appropriate extraction of LG involving various parameters to achieve a high yield and purity LG is very necessary.

Studies are widely conducted on extraction and application of LG, reports have rarely investigated the qualitative and quantitative approaches of LG. It was only Li and Zhuang used HPLC and TLC to simply analyze LG qualitatively [7,17], lacking of fully qualitative and quantitative analyses for LG.

In this research, cotton straw was selected as feedstock for bio-oil production. The aims of this study were (i) determining the effects of pyrolysis temperature, particle size, holding time and acid concentration on LG yield, and (ii) using response surface technique to optimize parameters to extract LG from cotton straw bio-oil, and (iii) quantitatively and qualitatively investigating the test parameters of LG by using HPLC, FTIR and NMR.

2. Materials and methods

2.1. Materials

Air-dried samples of cotton straw were shredded and sieved into five particle size ranges: 300–350, 600–650, 900–950, 1200–1250, and 1500–1550 μm . The samples were then dried in an oven at 80 °C until a constant weight was reached. All the samples were stored in sealed containers in a cool and dark indoor environment. The amount of samples used for each pyrolysis experiment was 15–20 g. Table 1 shows the main characteristics of the cotton straw used (lignocellulosic composition and ash content).

The chemicals, such as pyridine (AR), acetic anhydride (AR), chloroform (AR), methyl isobutyl ketone (MIBK, AR), hydrochloric acid (AR), and ethyl acetate (EtOAc, AR) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (Tianjin, China). The standard LG and other chromatographic reagents (with purities > 99%) were purchased from Sigma Chemical Company (Beijing, China). High purity water was produced by Milli-Q system (Millipore, Bedford, MA, USA). Granular activated carbon (GAC) was made by our research group with a surface area of 716.6 m^2/g . All solvents and samples were filtered through 0.22 μm filter before injection.

2.2. Pyrolysis procedure

Fast pyrolysis was conducted in a fluidized bed reactor that has been reported elsewhere [18]. Detail information of reactor system is shown in Fig. 1. The fluidized bed reactor has a height of 1 m and a diameter of 70 mm, in which cotton straw is rapidly heated for pyrolysis. The reactor was heated externally by an electric heater, which can pre-heat the nitrogen to the temperature range of 400–600 °C before entering into the fluidized bed reactor. In this study, the condensation temperature was set at ice water bath for all experiments. In order to build a significant descriptive pyrolysis model of obtaining more LG from bio-oil, several series were carried out. The first series of experiments were carried out to determine the effect of the temperatures on LG yields with a constant particle size of 600–650 μm , 8% of acid washing (hydrochloric acid, HCl), 1.4 s of holding time. Fast pyrolysis of cotton straw was carried out in the temperature range of 400–600 °C at intervals of 50 °C. After experiment, the solid char was removed from inside reactor and the bio-oil and LG yields were calculated as follows:

$$\text{Yield} = [\text{Desired product (g)}/\text{Cotton straw (g)}] \times 100\% \quad (1)$$

$$\text{Yield} = [\text{Desired product (g)}/\text{Bio - oil (g)}] \times 100\% \quad (2)$$

The content of LG was measured on high performance liquid chromatography (HPLC) equipped with an evaporative light scattering detector. The obtained LG was washed three times by 95% alcohol with continuing whisking for 15 min, and then centrifuging (5000 rpm) for 15 min and the centrifugal residue was dissolved in 10.0 mL of water. All solutions (including standard LG sample) were filtrated by a 0.22 μm membrane filter before HPLC analysis. The HPLC system was recorded with an XBridge TM Amide C18 column (4.6 \times 250 mm, 3.5 μm), the mobile phase was methanol: water (9:1, v/v) at a flow rate of 0.5 mL/min. The temperature of the column was 25 °C and the injected volume was 5 μL . The gas flow was 40 psi, the drift tube was set to 75 °C and the sprayer was heated 60%.

The second series of experiments were performed to investigate the effect of particle sizes on the LG yield. For this set of experiments, the pyrolysis process conditions were kept in a constant temperature of 500 °C, 8% of acid washing and 1.4 s of holding time. The third series of experiment were carried out to study the effect of holding times on the LG yields. The durations of holding time were performed between 1.4 s and 6.8 s, which were adjusted by the nitrogen gas flow rates. The last group of experiments was performed to study the effects of acid washing on the LG yields. Cotton straw samples were treated with different concentrations of HCl by ultrasonic oscillation for 1 h with constant stirring: 0* (without washing), 0 (distilled water), 4%, 8%, 12% and 16%. After stirring, samples were washed with distilled water, and then filtered, dried and stored for use.

For all these four series of experiments to obtain maximum LG, the pyrolysis temperature, the particle size, the acid washing concentration and the holding time were kept constant 500 °C, 600–650 μm , 8% and 1.4 s, respectively.

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