



Characteristics and deoxy-liquefaction of cellulose extracted from cotton stalk



Jinhua Li^a, Shuai Zhang^a, Boyang Gao^a, Aikai Yang^a, Zonghua Wang^{a,*}, Yanzhi Xia^a, Haichao Liu^b

^a College of Chemical Science and Engineering, Teachers College, Collaborative Innovation Center for Marine Biomass Fiber Materials and Textiles, Qingdao University, Qingdao 266071, China

^b Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

HIGHLIGHTS

- Cellulose extracted from cotton stalk showed representative cellulose structure.
- The extracted cellulose was converted into liquid oil by deoxy-liquefaction.
- The liquid oil was mainly composed of aromatics, phenols, and alkanes.
- The liquid oil had low oxygen content and high heating values.

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ABSTRACT

Cellulose was extracted from cotton stalk and characterized by using scanning electron microscope (SEM), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) spectroscopy. The results showed that the extracted cellulose had representative cellulose structure. Furthermore, the extracted cellulose was converted into liquid oil by direct deoxy-liquefaction. The elemental analysis, FTIR spectroscopy and gas chromatography–mass spectrometry (GC–MS) analyses of the liquid oil indicated that the extracted cellulose oil was mainly composed of aromatic hydrocarbons, phenols and alkanes. This oil featured high quality including the low oxygen content of 6.46% and the higher heating value (HHV) of 42.66 MJ/kg. This suggested that deoxy-liquefaction technique may be an effective way to convert cellulose into high-quality liquid fuel and value-added chemicals.

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1. Introduction

Lignocellulose, as the most abundant and renewable source, has proved to be a potential feedstock to produce fuel and value-added chemicals [1,2], which is mainly composed of three basic structural components: cellulose, hemicellulose and lignin. Generally, dry lignocellulose is roughly comprised of 40–50% cellulose, 20–30% hemicellulose, and 20–35% lignin [3]. Obviously, cellulose is the most abundant component in lignocellulose, which consists of D-glucose units linked by 1,4-β-glycosidic bonds [3]. In practice, cellulose can be converted into useful chemicals such as mannitol [4], furfural [5], and levoglucosone [6], or fuels including cellulosic ethanol [3] and bio-oil through pyrolysis [1,2]. For example, Wang et al. [7] and Shen et al. [8] similarly investigated the main products from cellulose pyrolysis which were mainly composed

of levoglucosan, furfural, furans, hydroxyacetaldehyde, hydroxyacetone, etc. Obviously, the bio-oils obtained from cellulose by pyrolysis were highly oxygenated complex mixtures, which usually led to lower HHV and poor combustion properties. Furthermore, most of the above researches were performed on the commercially available microcrystalline cellulose, which is different from that extracted from lignocellulosic biomass.

In this paper, direct deoxy-liquefaction which has been proved to be effective to produce high-quality liquid oils from biomass [9–11] was applied to the thermochemical conversion of cellulose extracted from cotton stalk. During the conversion process of biomass, cellulose degradation was accompanied by the degradation of hemicellulose and lignin, which made the process more complicated. So it is necessary to separate the main component–cellulose from lignocellulosic biomass and study its degradation products. Up to date, various kinds of separation methods such as steam explosion, microwave assisted extraction, inorganic acid treatment, alkali treatment and ionic liquid methods have been reported. Recently, for example, Dong et al. [12], obtained cellulose

* Corresponding author. Tel.: +86 0532 85950873; fax: +86 0532 85955529.

E-mail address: wangzonghua@qdu.edu.cn (Z. Wang).

fibers from cotton stalk bark by a combination of steam explosion, potassium hydroxide and peroxide treatments. Differently, El-Sakhawy et al. [13] used hydrochloric or sulfuric acid to prepare microcrystalline cellulose from bagasse, rice straw and cotton stalk. While Song et al. [14] applied H_2SO_4 , NaOH and H_3PO_4 to decompose lignocellulose samples (giant reeds, pennisetum and cotton stalks) and investigated the correlation between cellulose allomorphs. In this study, cellulose was extracted from cotton stalk by using hydrochloric acid and sodium hydroxide to remove hemicellulose and lignin, which was the most simple and economic method. Furthermore, this cellulose was characterized and converted into liquid oil by direct deoxy-liquefaction. Then, the liquid oils obtained from extracted cellulose and cotton stalk feedstock were analyzed using elemental analysis, FTIR and GC–MS analyses.

2. Materials and methods

2.1. Materials

The sample of cotton stalk investigated in this study was collected from Shandong Province, China. Before the experiments, the sample was air-dried, grounded and then sieved to give fractions with particle size of 60 meshes. The determination of extractives, cellulose, hemicellulose, lignin and ash was based on Van Soest method [15]. And the characteristics of the samples on dry basis were shown in Table 1.

2.2. Extraction of cellulose

The cotton stalk powder was treated by refluxing in a Soxhlet apparatus with toluene-ethanol (2:1 v/v) for 6 h to remove fats and waxes and then dried in an oven under 110 °C for 8 h. The dried cotton stalk powder was added to 2 N HCl in a three-necked flask with magnetic stirring at 40–60 °C for 3–4 h. The reaction mixture was then filtered and the filter residue was washed repeatedly with distilled water to neutral. Finally, the above washed filter residue was delignified with 3% aqueous sodium hydroxide at 120 °C in autoclave for 2 h [16].

2.3. Experimental procedure

The direct liquefaction experiments were performed in a stainless steel tubular reactor with 15% water as medium, which is similar to the methods described in the literatures [10,11,17]. The reactor was heated at the heating rate of 80 °C/min and maintained for 30 min at final temperature of 400 °C. After heated, the reactor was cooled to room temperature and the volatile products were collected by gas collecting bags. Then, the residue was further distilled with the temperature rising from room temperature to

500 °C to obtain the liquid oil. Water was also distilled out and the oil floated on the water. When distillation finished, water was separated by an injector. Finally, the solid char was removed and weighed at room temperature. At least three duplicate runs were conducted, and the maximum error under the same conditions was ensured within 5%.

2.4. Analysis methods

The heating value was obtained by calculation according to Dulong's formula [18].

$$HHV \text{ (MJ/kg)} = [338.2 \times C \text{ wt\%} + 1442.8 \times (H \text{ wt\%} - O \text{ wt\%/8})] \times 0.001$$

Elemental analyses (C, H, and N) of the raw material and oil were performed on an elemental analyzer (Elemental Varian EL, Germany). The oxygen content was calculated by difference as follows:

$$O \text{ (wt\%)} = 100 - (C + H + N) \text{ (wt\%)}$$

FTIR spectra of extracted cellulose, cotton stalk and the liquid oil from cellulose were recorded using a Fourier-Transform Infrared Spectrometer (Varian 3100, America) over a range 4000–400 cm^{-1} . X-ray diffraction patterns of extracted cellulose and cotton stalk were carried out on a D8 Advance instrument (Bruker AXS, Germany) with Cu $K\alpha$ radiation and 2θ from 3° to 70°. Scanning electron microscope (SEM) images of extracted cellulose and cotton stalk were performed on a FESEM S-4800 (Japan). Cross polarization/magic angle spinning (CP/MAS) ^{13}C solid-state nuclear magnetic resonance (NMR) experiments were performed for the extracted cellulose and cotton stalk on a Bruker Advance III 400 NMR spectrometer operating at 25 °C.

The compositions of the liquid oils were analyzed by a Shimadzu gas chromatography and mass spectrometry (GC–MS) (QP2010S, Japan). The GC was fitted with a 30 m \times 0.25 mm \times 0.25 μm fused quartz capillary column and coated with TR-5MS as the stationary phase. Compounds in the oils were identified by comparison with the mass spectra with the NIST (National Institute of Standards and Technology) 08 library, together with the literature data to obtain the highest likelihood of compound identification.

3. Results and discussion

3.1. Characterizations of extracted cellulose

3.1.1. Scanning electron microscopy (SEM)

The cotton stalk and extracted cellulose was characterized using SEM to understand its surface morphology. From Fig. 1a and b, it can be seen that the grounded cotton stalk had a rough and non-uniform outer surface. The outer layer of the stalks was mostly composed of lignin, ash and hemicellulose that enclosed the interior cellulose. Most of these surface substances were removed during cellulose extraction resulting in relatively smooth cellulose as shown in Fig. 1c [19,20]. The extracted cellulose displayed a rod-shaped morphology with some of the crystalline regions broken in Fig. 1c, which was different from the images of the cellulose fibers in the literatures [14,21]. Fig. 1d shows irregular aggregated fiber fragments, a network structure and a rough surface morphology which may be attributed to the residual non-cellulose components such as hemicellulose and lignin [22,23].

3.1.2. X-ray diffraction (XRD)

As shown in Fig. 2, the XRD patterns of the extracted cellulose had similar diffraction peaks to those of cotton stalk. Compared

Table 1
Main characteristics of cotton stalk and the extracted cellulose oil.

Ultimate analysis	Cotton stalk	Liquid oil
C (wt%)	42.31	82.12
H (wt%)	6.19	11.16
O (wt%)	50.54	6.46
N (wt%)	0.81	0.22
Empirical formula	$CH_{1.75}O_{0.90}N_{0.016}$	$CH_{1.63}O_{0.06}N_{0.002}$
H/C molar ratio	1.75	1.63
O/C molar ratio	0.90	0.06
HHV (MJ kg^{-1})	14.12	42.66
Extractives (wt%)	5.61	
Cellulose (wt%)	41.83	
Hemicellulose (wt%)	24.53	
Lignin (wt%)	21.24	
Ash (wt%)	6.79	

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