Influence of solid alkali application on corn stalk dissolution and degradation in solvent systems

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ABSTRACT

In our study, solid alkali were produced and characterized by a series of methods. Dissolution of corn stalk was achieved in solvent systems at 170 °C for 5 h by cooking with solid alkali. The components of ionic liquid and water in solvent systems showed synergistic effects on lignocellulosic dissolution and degradation. Alkaline molecular sieves were proven to be the most effective solid alkali for lignin degradation, which promoted the dissolution efficiency of the corn stalk in solvent systems. Under the combined action of solid alkali and the nucleophilic component in solvent systems, lignin and hemicellulose in corn stalk were degraded. It effectively enhanced cellulose solubilization in solvent systems. The regenerated cellulose was demonstrated to be similar to microcrystalline cellulose according to Fourier Transform infrared spectroscopy and Nuclear Magnetic Resonance analyses. X-ray diffraction curves showed that the crystallinity of the regenerated cellulose is lower than that of microcrystalline cellulose.

1. Introduction

Interest in utilizing renewable energy to produce valuable products has attracted increasing attentions over the past several decades. Plants produce 100 billion tonnes of cellulose by photosynthesis annually, which is regarded as an inexhaustible and renewable resource [1,32]. Although the biochemical conversion of biomass into energy and industrial raw materials has significant technical and economic potential, lignocellulosic biomass is naturally resistant to chemical degradation. This resistance is due to various physical and chemical factors such as the presence of lignin, the crystallinity of cellulose and the presence of covalent cross-linkages between lignin and hemicelluloses in the plant cell wall [24,30].

Various biomass pretreatment and extraction techniques have been studied for the utilization of lignocellulosic biomass [12]. However, these technologies commonly use soluble acidic or basic chemicals and result in pollution. Nowadays, novel treatment methods utilizing green processes are studied. The application of solid alkali has been a focus of recent studies on biomass treatment

[21,28]. Researchers have attempted to use an insoluble Mg-based solid alkali in place of soluble alkali to provide a new delignification medium [5]. For example, Mg-based solid alkali was introduced in a novel method of cooking corn stalk with active oxygen for pulp production. Separately, extensive research into the use of ionic liquids as a new kind of green solvent has been conducted [6]. Ionic liquids have unique physical and chemical properties, such as low melting point (up to 173 K), higher solubility, and designable selective dissolution. Ionic liquids offer a variety of advantages permitting their use in chemical synthesis, extraction and separation, materials preparation and other fields [16]. In the last decade or so, several ionic liquids capable of dissolving cellulose have been reported [17]. BMIMCl is a nonvolatile, strong solvent for cellulose and is easily recovered after processing. These attributes prompted further research on the regulation and design of cation—anion structures to obtain new types of ionic liquids with superior properties. The allyl group was also introduced to the cationic structure of an ionic liquid to prepare 1-allyl-3-methylimidazolium chloride (AMIMCl), which has excellent solvent properties.

In the present study, solid alkali were produced and characterized by a series of methods. Dissolution of corn stalk was achieved in solvent systems at 170 °C for 5 h by cooking with solid alkali. We also studied the influence of various parameters in the cooking process on corn stalk dissolution and degradation. The regenerated

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cellulose was characterized by Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) analyses. This paper provides the necessary theoretical basis for the application of solid alkali for the utilization of biomass feedstock resources.

2. Materials and methods

2.1. Materials

Samples of corn stalk were collected from agricultural fields in Tianjin in northern China. After drying at 60 °C in an oven for 16 h, the samples were ground to particles that passed through a 0.7 mm screen. The fiber components of corn stalk were analyzed according to the Van Soest method using a FOSS Fibertec 2010 fully automated fiber analysis system. This analysis revealed the following composition: lignin, 13.87% (w/w); hemicellulose, (w/w); 28.01% cellulose, 40.86% (w/w).

Microcrystalline cellulose was purchased from Serva (Heidelberg, Germany). MgO powder (purity 99.95%), Al_2O_3 powder (purity 99.97%) and SBA-15 molecular sieve powder (purity 99.97%) were purchased from Tianjin Xuanyang (Tianjin, China). 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-allyl-3-methylimidazolium acetate (AMIMOAc) were purchased from Shanghai Kefeng (Shanghai) Trading Co., Ltd., Shanghai, China.

2.2. Preparation of solid alkali

MgO powder and SBA-15 molecular sieve powder were mixed in deionized water and wet ball-milled to decrease the particle size. The mass ratio of MgO powder and SBA-15 molecular sieve powder was set at 1:10 [21]. The mixture was then heated for 5 h at 105 °C to remove the water. The powder obtained was sintered at 550 °C for 6 h to produce alkaline molecular sieves. This method was also used for alumina-doped MgO preparation.

2.3. Preparation of solvent systems

The solvent systems employed to dissolve corn stalk were prepared by directly mixing deionized water and ionic liquids at room temperature. The mass ratio of deionized water to ionic liquids was set at 0, 5%, 10%, 15%, 20%, 25% and 30%. Solvent system containing deionized water and AMIMCl was denoted as S_1. The other system contained water and AMIMOAc, denoted as S_2.

2.4. Corn stalk cooking

Corn stalk was loaded into a stainless reactor charged with 20 ml of solvent systems and treated with solid alkali at 170 °C for 5 h. When the reactor was cooled to room temperature, the mixture was filtered with a Buchner funnel to separate treated corn stalk from the filtrate. The treated corn stalk was washed with deionized water, then filtered through a nylon membrane and air-dried.

The Van Soest method, commonly used to analyze the constitution of lignocelluloses, was used to measure the lignocellulose content in corn stalk. First, 100 ml of neutral detergent, 0.5 g of Na_2SO_3 and several drops of octanol mixed with 1.0 g of sample were kept boiling for about 1 h. Then the solution was filtered and washed several times. The precipitate was dried and weighed (W_1). Second, the precipitate was refluxed with 100 ml of acidic detergent for 1 h. After filtration, the precipitate was washed three times with hot water. After that the precipitate was dried and weighed (W_2). Third, the precipitate was mixed with 10 ml of 72% sulfuric acid for digestion overnight. Then the precipitate was washed and filtered. After being dried, the precipitate was weighed (W_3).

Finally, the precipitate was incinerated at 550 °C for 4 h. After cooling, the ash was weighed (W_4). The contents of various components were calculated as mentioned in Van Soest method [14].

Corn stalk samples treated with solid alkali are denoted as follows: C_1 (corn stalk treated with alkaline molecular sieves in solvent system S_1), C_2 (corn stalk treated with alumina-doped MgO in solvent system S_1), C_3 (corn stalk treated with MgO in solvent system S_1), C_4 (corn stalk treated without solid alkali in solvent system S_1), C_1' (corn stalk treated with alkaline molecular sieves in solvent system S_2), C_2' (corn stalk treated with alumina-doped MgO in solvent system S_2), C_3' (corn stalk treated with MgO in solvent system S_2) and C_4' (corn stalk treated without solid alkali in solvent system S_2). The lignocellulose residual rate was calculated according to Eqn. (1) [14]:

$$R_{s,i} = \frac{M_{r,i}}{M_{o,i}} \quad (1)$$

where i represents cellulose, hemicellulose or lignin; $R_{s,i}$ is the residual rate; $M_{r,i}$ is the mass of the residual cellulose, hemicellulose or lignin in the corn stalk sample after cooking; $M_{o,i}$ is the mass of cellulose, hemicellulose or lignin in the original corn stalk sample.

The resulting filtrate was collected to regenerate cellulose. The solubility of the sample in solvent was calculated as shown in Eqn. (2) [14]:

$$R_d = 1 - \frac{M_r}{M_o} \quad (2)$$

where R_d is the solubility in solvent system; M_r is the mass of the residual sample after cooking; M_o is the mass of the original sample.

2.5. Regeneration of cellulose

The residues in the filtrate were extracted with ethyl acetate at room temperature. The extracted residues were defined as degraded corn stalk: DCS_1 (residues in the filtrate separated from C_1), DCS_2 (residues in the filtrate separated from C_2), DCS_3 (residues in the filtrate separated from C_3), DCS_4 (residues in the filtrate separated from C_4), DCS_1' (residues in the filtrate separated from C_1), DCS_2' (residues in the filtrate separated from C_2), DCS_3' (residues in the filtrate separated from C_3), and DCS_4' (residues in the filtrate separated from C_4).

After extraction with ethyl acetate, the resulting filtrate, containing primarily cellulose, was combined with excessive deionized water to regenerate the cellulose. The regenerated cellulose samples were dried at 80 °C for 72 h. The cellulose regeneration rate was calculated as shown in Eqn. (3) [14]:

$$R_r = \frac{M_{r-cel}}{M_{o-cel}} \quad (3)$$

where R_r is the cellulose regeneration rate; M_{r-cel} is the mass of regenerated cellulose from filtrate; M_{o-cel} is the mass of cellulose in the original corn stalk.

The measurements mentioned in Section 2.5 and 2.6 were repeated 5 times in order to guaranty the credibility and accuracy of measured data.

2.6. Characterization

2.6.1. XRD

The crystal structure of the alkaline molecular sieves was studied using an XRD analyzer (Rigaku D/max-III X-ray