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Short Communication

Black liquor-derived carbonaceous solid acid catalyst for the hydrolysis of pretreated rice straw in ionic liquid

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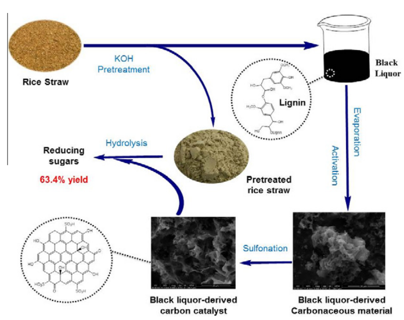
HIGHLIGHTS

- Carbonaceous solid acid catalyst was prepared from rice straw-derived black liquor.
- KOH acting as both lignin extracting agent and activation agent of carbon material.
- The solid acid catalyst showed good activity for hydrolysis of pretreated rice straw.
- A maximum TRS yield of 63.4% was obtained from the KOH pretreated rice straw.
- A renewable strategy for utilization of all components of lignocellulosic biomass.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignin-containing black liquor from pretreatment of rice straw by KOH aqueous solution was applied to prepare a carbonaceous solid acid catalyst, in which KOH played dual roles of extracting lignin from rice straw and developing porosity of the carbon material as an activation agent. The synthesized black liquor-derived carbon material was applied in catalytic hydrolysis of the residue solid from the pretreatment of rice straw, which was mainly composed of cellulose and hemicellulose, and showed excellent activity for the production of total reducing sugars (TRS) in ionic liquid, 1-butyl-3-methyl imidazolium chloride. The highest TRS yield of 63.4% was achieved at 140 °C for 120 min, which was much higher than that obtained from crude rice straw under the same reaction conditions (36.6% TRS yield). Overall, this study provides a renewable strategy for the utilization of all components of lignocellulosic biomass.

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1. Introduction

As the most widespread biomass on the earth, investigation of the conversion of lignocellulosic biomass to various chemicals and biofuels has been receiving increased attention in the last few decades since they have great potential to replace traditional fossil fuels and provide a variety of chemicals and biofuels (Yabushita et al., 2014). Rice straw, which is one of the most important lignocellulosic agricultural wastes, mainly consists of cellulose, hemicellulose and lignin. Generally, rice straw is burned or discarded in the field because of a shortage of cost-effective reclamation methods, which has led to serious environmental pollution issues (Singh et al., 2016). Because rice straw has high contents of cellulose (33–47%) and hemicellulose (19–27%) (Singh et al., 2016), it is a promising starting material that can be employed to prepare platform chemicals and biofuels such as ethanol and butanol, mainly via biological conversion processes.

From the aspect of the reaction pathway, the transformation of lignocellulose into biofuels or chemicals mainly involves two stages, hydrolysis of cellulose and hemicellulose into reducing

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sugars, and the subsequent conversion of these sugars into chemicals and biofuels such as ethanol through fermentation methods. Since cellulose and hemicellulose are tightly covered by impermeable lignin layers, pretreatment procedures such as physical, chemical or biological processes are normally essential to the enzymatic hydrolysis of lignocellulosic biomass because they remove or reduce its recalcitrance contributed from lignin and increase the accessibility of the pretreated substrate (Dai et al., 2015; Li et al., 2016). Among these pretreatment approaches, alkali sodium hydroxide (NaOH) has been the most widely applied for many years because it can efficiently disrupt and separate lignin fraction, and thus increase the accessibility of cellulose and hemicellulose to enzymes (Narra et al., 2016). During NaOH pretreatment, most of the lignin and part of the hemicellulose in lignocellulose dissolve in NaOH aqueous solution to form black liquor, while the remaining solid, which mainly consists of cellulose and hemicellulose, enter a biorefinery process in which cellulose and hemicellulose can be transformed into ethanol or other chemicals via a hydrolysis step.

The hydrolysis of cellulose is a key procedure in biorefinery industry for transforming lignocellulosic biomass into a variety of value-added chemicals. Enzymes and mineral acids have long been used to depolymerize cellulose. Although enzymes can efficiently hydrolyze cellulose to glucose, they are expensive and require a long reaction time. Mineral acids can hydrolyze cellulose rapidly, but they cause corrosion, a large amount of acid-waste generation and environmental pollution (Binder and Raines, 2010; vom Stein et al., 2010). In addition, both enzymes and mineral acids are difficult to recover and recycle from the reaction system (Qiu et al., 2012; Ramakrishnan et al., 2010). Conversely, solid acid catalysts are receiving increasing attention because of their advantages such as satisfied efficiency, appropriate reaction time, environmental friendliness and recyclability. Various solid acids have been used for cellulose hydrolysis, including ion-exchange resin (Meena et al., 2015; Qi et al., 2011), layered transition-metal oxides (Lai et al., 2011), heteropolyacids (Tian et al., 2010), and sulfonated carbons (Foo and Sievers, 2015; Wu et al., 2010). Among these solid acids, carbon catalysts have drawn a great deal of attention because they can be prepared from the biomass itself, and they show good catalytic performance (Fukuhara et al., 2011).

In this work, rice straw was pretreated with KOH aqueous solution to remove lignin and increase the accessibility of the remaining cellulose and hemicellulose components for further treatment. The generated black liquor, which primarily consisted of lignin, was then used as a precursor to prepare porous carbonaceous solid acid. For this step, KOH acted as both an extractant of lignin and activation agent to prepare porous carbon. The as-synthesized carbonaceous solid acid was then applied to hydrolyze the pretreated rice straw, which mainly consisted of cellulose and hemicellulose in ionic liquid solvent, and exhibited good catalytic activity. The process proposed herein provides a renewable method for all components utilization of lignocellulosic biomass.

2. Experimental methods

2.1. Materials

Ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) (purity 99%) was provided by Henan Lihua Pharmaceutical Co., Ltd. (Xinxiang, Henan). Rice straw containing 33% cellulose and 19% hemicellulose was obtained from Xiangtan (Hunan, South China). Potassium hydroxide and sulfuric acid (99%) were purchased from Alfa Aesar Company.

2.2. Pretreatment of rice straw and preparation of carbonaceous solid acid catalyst

Dried rice straw was ground to pass through a 40 mesh sieve before use. The ground rice straw powder (15 g) was then immersed into 120 mL 6% KOH aqueous solution and loaded into a 200 mL Teflon lined stainless steel autoclave, which was then allowed to heat for 4 h at 120 °C in an oven. Next, the autoclave was cooled and the residual solid material was filtrated from the mixture. The collected solid material was subsequently rinsed thoroughly with ultra-pure water until the filtrate was neutral, dried, and utilized for the hydrolysis stage. The cellulose and hemicellulose in the rice straw pretreated with KOH was determined to be 63% and 17%, respectively.

After filtration, the lignin-containing black liquor was evaporated at 80 °C to remove water until it became a solid composite consisting primarily of lignin and KOH. This material was then pyrolyzed and chemically activated in a horizontal tubular furnace under nitrogen gas at 400 °C for 1 h, followed by 600 °C for 2 h. Next, the resulting carbonaceous sample was rinsed with HCl aqueous solution (1 M) and ultra-pure water repeatedly until the leachate became neutral. After drying at 80 °C in a vacuum oven for 12 h, the obtained carbonaceous material (denoted as BLCM) (10 g) was heated in 20 mL concentrated H_2SO_4 at 150 °C for 10 h under N_2 to introduce –SO_3H groups onto the carbonaceous material. Finally, the resulting solid was rinsed with ultra-pure water till no SO_4^{2-} ions were detected in the eluent, followed by drying at 80 °C for 12 h (denoted as BLSCM).

2.3. Characterization of the prepared carbonaceous material

The synthesized carbonaceous material was characterized by SEM (QUANTA250, FEI), FT-IR (5700 FT-IR Spectrometer, NICOLET), X-ray diffraction (D8 Advance LynxEye Detection, Bruker), elemental analysis (VARIO EL CUBE, Elementar), Brumauer-Emmett-Teller (BET, Quantachrome Instruments Quadrasorb SI) and ICP (ICP-9000, Thermo Jarrell-Ash Corp., USA) techniques.

2.4. Hydrolysis of rice straw

Typically, reaction mixture was prepared by adding 0.05 g rice straw pretreated with KOH aqueous solution into 1 g of [BMIM][Cl], following with addition of 0.05 g water and 0.05 g carbon catalysts. The reaction mixture was subsequently heated to a given reaction temperature in an oil bath in a closed reactor for a certain reaction time. After reaction, the solid was separated by filtration, and the obtained liquid sample was diluted with ultra-pure water and analyzed by using the 3, 5-dinitrosalicylic acid (DNS) method to determine the total reducing sugars (TRS) in the products (Li et al., 2008). The TRS yields were calculated using Eq. (1):

$$\text{TRS yield (mol\%)} = \frac{\text{moles of the produced reducing sugars in production}}{\text{Theoretical moles of glucose and xylose unit in the loaded sample}} \times 100\% \quad (1)$$

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