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Efficient production of glucose by microwave-assisted acid hydrolysis of cellulose hydrogel

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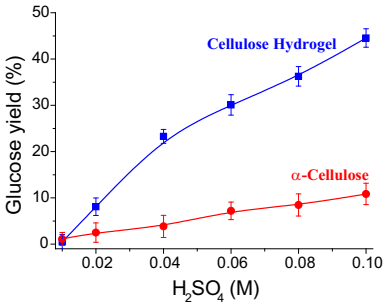
HIGHLIGHTS

- Regenerated cellulose hydrogel was prepared and efficiently hydrolyzed by acid.
- Ozone treatment of cellulose solution further enhanced the yield of glucose.
- The method is effective for α-cellulose, microcrystalline cellulose and natural fibers.
- Fresh and used celluloses were characterized to understand the hydrolysis mechanism.

GRAPHICAL ABSTRACT

The hydrolysis of cellulose hydrogel is greatly improved compared with cellulose powder.



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ABSTRACT

To improve the production of glucose from cellulose, a simple and effective route was developed. This process uses a combination of a step of cellulose dissolution in aqueous NaOH/urea solution and then regeneration with water, followed by an acid hydrolysis step under microwave irradiation. The method is effective to obtain glucose from α-cellulose, microcrystalline cellulose, filter paper, ramie fiber and absorbent cotton. Increased with the acid concentration the glucose yield from hydrogel hydrolysis increased from 0.42% to 44.6% at 160 °C for 10 min. Moreover, the ozone treatment of cellulose in NaOH/urea solution before regeneration significantly enhanced the hydrolysis efficiency with a glucose yield of 59.1%. It is believed that the chains in cellulose hydrogel are relatively free approached, making that the acids easily access the β-glycosidic bonds.

1. Introduction

Cellulose, the most common natural organic polymer, is considered as an almost inexhaustible source of raw material for the increasing demand for environment friendly and biocompatible products. Conversion of cellulose is of vital importance in the biofuel industry. Over the past years, much work has focused on developing effective technologies for acid hydrolysis of cellulose to glucose (Huang and Fu, 2013; vom Stein et al., 2010; Zhang and Lynd, 2004). A variety of pretreatment methods also have been developed to its activation prior to catalytic hydrolysis, mainly including physical pretreatment such as ball-milling (Zhao et al., 2006), non-thermal atmospheric plasma (Benoit et al., 2011), solvent pretreatment such as ionic liquids (Qu et al., 2014), dilute acids (Chimentao et al., 2014) and concentrated acids (Ni et al., 2013). But clearly, it is desirable to develop a simple, green, and

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low-cost route to treat cellulose and perform the catalytic conversion in a more rational way.

The degradation of cellulose aggregations is step-by-step from the surface to inner, resulting in a slow depolymerization rate. Solving of cellulose will be helpful to the hydrolysis as the cellulose chains are free approached in these forms. It is well-known that cellulose is difficult to be dissolved in the common solvent for the existence of crystalline structure of complex hydrogen-bonding network. Recently, a new class of cellulose solvent has been developed, namely, aqueous solutions of NaOH or LiOH and urea used at low temperatures (Cai and Zhang, 2005). Under optimized conditions, these solutions can readily dissolve even highly crystalline cellulose; and the regeneration of cellulose from the solvents gives highly transparent cellulose hydrogels (Chang et al., 2010). Usually, hydrogels are chemically or physically crosslinked structures composed of hydrophilic polymers in a three dimensional network. The hydrolysis of cellulose hydrogel in the presence of a catalyst could be enhanced due to the exposure of more reaction sites and much easier diffusion of the catalyst into the cellulose molecular. Thus, it provides a chance to obtain high-value chemicals from the material. However, the acid hydrolysis of cellulose in its hydrogel form has scarce reports until now. The present work is aimed at investigating the hydrolysis of cellulose hydrogel to glucose with diluted sulfate acid as the catalyst. As microwave heating presents a potentially fast, efficient, and selective method for the thermal treatment of biomass in the last decade, the hydrolysis reaction was performed in a microwave accelerated reaction system.

2. Methods

2.1. Materials

α-Cellulose with an average particle size of 50 μm, levulinic acid (LA), 5-hydroxymethyl-2-furaldehyde (HMF) and furfural were supplied by Aladdin Reagent. Microcrystalline cellulose, H_2SO_4, NaOH, ethanol, Na_2CO_3, potassium ferricyanide and filter paper were purchased from Sinopharm Chemical Reagent. Glucose assay kits were obtained from Changchun Huili Biotech. Co., Ltd. Absorbent cotton was purchased from Shanghai Dai Di Medical Instrument Co., Ltd. and used as cotton fiber. Ramie fiber was purified by alkali treatment of ramie bark after degumming. Deionized water was used throughout the experiment.

2.2. Dissolution and regeneration of cellulose

Cellulose solution was prepared from aqueous NaOH/urea solution similar to the reported literature (Cai and Zhang, 2005). The treated cellulose sample was then repeatedly washed with a large amount of distilled water, until the pH of the supernatant became neutral. An aliquot of the washed sample was kept in the wet state until required for use, while the rest of the washed sample was air dried at room temperature. 5 wt% H_2SO_4 aqueous solution and ethanol were also used to obtain the hydrogel instead of water.

2.3. Cellulose characterization

Crystal structure and crystallinity of cellulose and hydrogel were measured with a Bruker D8 powder X-ray Diffractometer with Cu Kα radiation (λ = 0.15406 nm). The beam voltage and current used were 40 kV and 40 mA, respectively. The degree of crystallinity (Cr) was calculated by Cr = Fc/(Fc + Fa) × 100%, where, Fc and Fa are the areas of crystal and amorphous regions, respectively (Ni et al., 2013). The size and the morphology of hydrogel in the swollen state were evaluated by optical and environmental scanning electron microscopy (ESEM, FEI Quanta 200, Netherlands).

The average DP of different cellulose samples was measured viscosimetrically in 6 wt% NaOH/4 wt% urea aqueous solution using an Ubbelohde viscometer at 25 ± 0.1 °C (Zhou et al., 2004).

2.4. Microwave assistance hydrolysis

The experiments were carried out in a microwave digestion instrument (MDS-6, Sineo Microwave Chemistry Technology (Shanghai) Co., Ltd). Dilute sulfuric acid solution and cellulose hydrogel or cellulose powder, were putted into a 50 mL Teflon vessel and then heated by 1000 W microwave. The concentration of cellulose was 11.8 g/L. When the temperature reached to 160 °C within 10 min, the mixture was further kept heating for another 10 min. Each experiment was repeated in triplicate. After the reaction, the reaction mixture was filtered and the filtrate solution was analyzed for total reducing sugars (TRS) and glucose.

2.5. Analysis

A colorimetric method, potassium ferricyanide, was used to measure TRS as reported in a previous report (Li et al., 2009). Glucose was analyzed by a commercially available enzymatic glucose kit. Both of the calibration curves were recorded taking glucose as standard substrate. All samples were diluted until absorbance values were within the linear region of the curve. The yield of glucose and TRS were calculated as following: glucose yield (%) = the concentration of glucose (g/L)/the initial concentration of loaded cellulose (g/L) × 100; TRS yield (%) = the concentration of TRS (g/L)/the initial concentration of loaded cellulose (g/L) × 100; selectivity of glucose (%) = yield of glucose/converted cellulose × 100.

After reaction, the concentration of by-products such as LA, 5-HMF and furfural was conducted using a HPLC system (Agilent, USA, 1200 Series high-performance liquid chromatography) equipped with Zorbax Eclipse Plus C18 column and a UV–Vis Detector at 286 nm. The mobile phase consisted of 0.05 mol/L phosphate buffer solution (pH 2.6)–methanol (85:15, V/V).

3. Results and discussion

3.1. Characterization of RCH

The X-ray diffraction patterns were shown in Fig. S1. The spectrum for α-cellulose showed the characteristic sharp peaks of cellulose I at 14.8°, 16.3°, 22.6° and 34.5° (Ni et al., 2014). In contrast, RCH showed two broad peaks at around 29° and 41°, which was apparently resulted from scattering by liquid water. In addition, another very weak peak at 20° could be observed, indicating the presence of crystallization of cellulose II (Ni et al., 2014). Furthermore, the crystallinity (Cr) was calculated as 80.6% for α-cellulose, while the Cr in RCH was only 39.2%, significantly lower than that of α-cellulose. These results suggested that in the hydrogel the crystallization of cellulose I was mainly converted to amorphous cellulose with a minor amount of cellulose II. The X-ray diffraction spectrum for the air dried RCH at room temperature was also given in Fig. S1. Differently from the spectrum of the RCH, the peaks for amorphous cellulose diminished, and the strong typical peaks for cellulose II at 2θ of 11.9°, 20.0° and 21.8° appeared. The calculated Cr in the material was 69.6%, only slightly lower than that in α-cellulose. This behavior was caused by recrystallization of cellulose II when it was dried. Similar observations have been made for the dissolution of cellulose in other solutions such as phosphoric acid (Zhang et al., 2006) and ionic liquid (Qu et al., 2014). Thus, it was likely that all of the crystalline domains