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Hydrolysis of cellulose into reducing sugar via hot-compressed ethanol/water mixture

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ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form
8 March 2012
Accepted 9 March 2012
Available online 2 April 2012

Keywords:
Cellulose hydrolysis
Reducing sugar
Hot-compressed
ethanol/water mixture
Crystallinity index
Microcrystalline cellulose

ABSTRACT

Hydrolysis of cellulose by hot-compressed ethanol/water mixture is a promising way to obtain reducing sugar (RS) for biofuel production. The purpose of this research is to obtain high RS yield. In this work, the hydrolysis of microcrystalline cellulose by batch hot-compressed ethanol/water mixture was investigated. The influence of the ethanol/water mixture density corresponding to temperature and pressure on the RS yield was further examined. The hydrolysis conditions were optimized for high sugar yield and the crystallinity indexes (CI) of the residue and the original cellulose were analyzed. The RS yield reached as high as 98.22% under the conditions of ethanol mole fraction of 0.22, temperature of 260 °C, pressure of 5.75 MPa, reaction time of 35 s, and stirring speed of 10 Hz. The IR crystallinity index of cellulose was decreased to 0.211 from 0.618. It is shown that the RS can be produced effectively by cellulose hydrolysis in hot-compressed ethanol/water mixture.

1. Introduction

In recent years, renewable energy resources such as biofuels have attracted increasing attention due to the rapid increase of world energy demand and energy consumption [1–4]. Globally, the means to utilize this abundantly available resource in a cost-effective way is a major research focus. Biomass contributes about 12% of the global primary energy supply and up to 40–50% in many developing countries [5]. Cellulose, which is widely present in straw, bagasse, wood and other agricultural and forestry wastes, has been applied in industries of papers, fiber, foods, and chemicals, etc. However, it has not yet been fully utilized. To further utilize cellulose materials, such methods as liquefaction and gasification are essential [6,7]. For the conversion of cellulose into energy and chemical region, saccharification of cellulose and hemicellulose followed by fermentation is one of the methods to obtain ethanol which can be used not only as a useful chemical but also as a liquid fuel.

Thus, various methods such as enzymatic hydrolysis and acid hydrolysis as well as combination of both have been proposed and applied to hydrolyze lignocellulosic biomass as a way to recover saccharides [8–13]. In order to further optimize the hydrolysis process, subcritical and supercritical water treatments have also been investigated to obtain saccharides for subsequent fermentation to ethanol [14–21]. Firstly, Bobleter et al. [14] proposed the hydrothermal treatment of lignocellulose in subcritical water without catalyst.

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0961-9534/$ – see front matter
doi:10.1016/j.biombioe.2012.03.004

Sakaki et al. [15,16] reported that cellulose was rapidly decomposed to water-soluble compounds in near-critical water by a batch reactor, and yield reached nearly 80%. Sasaki et al. [18] conducted supercritical treatment of cellulose, and found that cellulose can be converted to water-soluble saccharides more effectively in supercritical water (>374 °C, >22.1 MPa) than in subcritical water. Saka and Ueno [22] reported that large amounts of glucose and levoglucosan can be obtained from cellulose in supercritical water. Ando et al. [23] examined the decomposition behavior of plant biomass in hot-compressed water using a semi-batch reactor. The result was that more than 95% of the charged amount of biomass materials could be decomposed by hot-compressed water. However, these hydrolyzed products are further decomposed into various volatile and gaseous compounds in the severe conditions of supercritical water [21].

The above-mentioned researches have made significant breakthroughs in the field of preparing saccharides from cellulose. Nevertheless, the techniques proposed are difficult to be applied in industrial production due to the high reaction temperature and pressure, and low saccharide yield caused by the degradation. Yamazaki et al. [24] reported alcohols with longer alkyl chains could dissolve macromolecules and liquefy lignocellulose rapidly in supercritical region. Thus, we proposed to prepare saccharides from cellulose hydrolysis by hot-compressed alcohol/water mixture. Due to the low critical temperatures and pressures of this conventional alcohols (methanol, T_c: 239.5 °C, P_c: 8.1 MPa; ethanol, T_c: 240.8 °C, P_c: 6.1 MPa; isopropanol, T_c: 235.2 °C, P_c: 4.8 MPa), the critical point and the dielectric constant of the alcohol/water mixture would be lower than that of pure water, which led to milder conditions for the reaction and the increase of the solubility of relatively high molecular weight products from cellulose, hemicelluloses, and lignin. Earlier works [25–28] have reported good conversion of lignocellulosic biomass into liquefied products by supercritical methanol treatment. However, up to now, few studies have been made on saccharides from cellulose hydrolysis by alcohol/water mixture treatment.

In this study, the chemical conversion of cellulose by hot-compressed alcohol/water mixture treatments was examined. The first goal of this work was to compare the hydrolysis of microcrystalline cellulose in different hot-compressed alcohol/water mixtures treatment, in which RS production was focused on. As a result, it was found that the ethanol/water mixture was the best one. Then an equation expressed the relationship between the RS yield and the density as well as the ethanol mole fraction in ethanol/water mixture system was proposed. Finally, the hydrolysis mechanism of cellulose in ethanol/water mixture was briefly discussed.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose powder (purity ≥ 99.7%; average particle diameter 20–80 μm; Product Number 061208) purchased from Le Tai Chemical Co., Ltd. was used throughout the experiment. Alcohols used in the entire experiment were analytic grade and purchased from the Tianjin Bodi Chemical Holding Co., Ltd.

2.2. Experimental procedures

Fig. 1 shows the experimental setup which consists of a feeding system, a preheating system, a reactor and product collection parts. The alcohol/water mixture in solvent tank were pressurized by a high-pressure pump and preheated in a tin bath heater to the designated temperature. Then, the preheated mixture was fed into an autoclave reactor which contains a certain amount of microcrystalline cellulose powder. Meanwhile, the heater in the reactor was turned on to keep the temperature constant. The thermocouples showed the temperatures of the inlet and interior in the autoclave during the experiment. The reaction time was counted after the inside temperature of the reactor reached the designated temperature. Water-soluble compounds which were produced by hydrolysis left the reactor as aqueous solution and were cooled in a condenser immediately. Samples were then collected. In the present study, the autoclave reactor was preheated to 75–85 °C and alcohol/water mixture at 200–280 °C were supplied.

2.3. Cellulose hydrolysis via hot-compressed alcohol/water mixtures

Microcrystalline cellulose was treated in different hot-compressed alcohol/water mixtures with various mole fractions by using methanol/water, ethanol/water or isopropanol/water as the solvent. Under the concentration of microcrystalline cellulose of 50 kg m^{-3}, mixture volume of 150 mL, reaction time of 35 s, stirring frequency of 10 Hz, and temperatures ranging from 200 to 280 °C, the hydrolysis of cellulose and the yield of RS were investigated. All the experiments were performed in duplicate, with the average value reported.

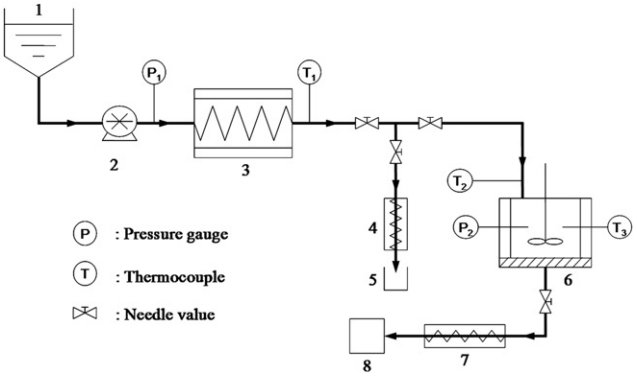

Fig. 1 – Schematic diagram of experimental setup: (1) solvent tank; (2) high-pressure pump; (3) tin bath heater; (4),(7) condenser; (5) waste liquid tank;(6) autoclave reactor; (8) collector.