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Multi-level dissolution and hydrolysis of lignocellulosic waste with a semi-flow hydrothermal system

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HIGHLIGHTS

- Multi-level hydrothermal process was studied to optimize lignocellulosic conversion.
- Semi-flow system offers separate and long residence times to undissolved materials.
- Dissolution of amorphous compounds at 195–200 °C without affecting cellulose.
- Cellulose dissolution ratios higher than 75% are achieved at 245–250 °C.
- Soluble sugars can be further obtained after the hydrolysis of dissolved cellulose.

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ABSTRACT

The hydrothermal process is efficient in lignocellulosic conversion and is beneficial to potential bioethanol production. In batch- and flow-type processes, concurrent dissolution and hydrolysis of lignocellulose result in product loss and inhibitory intermediates. Therefore, multi-level hydrothermal conversion of corn stalks was implemented with a semi-flow system to provide different residence times to undissolved compounds and facilitate dissolution or hydrolysis at respective optimal conditions. First-stage dissolution dissolved amorphous hemicellulose and lignin at 195–200 °C. Xylan, acid soluble lignin, and part of Klason lignin were dissolved without affecting glucan. In second-stage dissolution, the crystallinity of the undissolved materials suddenly decreased at 245–250 °C. The cellulose dissolution ratio was higher than 75%. Soluble sugars were obtained after the hydrolysis of dissolved cellulose at 280 °C. The results provide significant information on the multi-level hydrothermal process and its potential applications for recovering valuable chemicals from lignocellulosic waste.

1. Introduction

Biofuel production from biomass conversion has received increasing attention as a promising renewable energy that can overcome the disadvantages of fossil fuel, such as climate change and limited availability. As the most commonly produced biofuel in the world, bio-ethanol is traditionally obtained from food-based sources, such as agricultural crops with high contents of carbohydrates, which are facing the problem of competition for food requirement (Bommarius et al., 2008). As a result, interest in second-generation processes utilizing low-cost feedstock, such as lignocellulosic materials, has emerged (Sittijunda et al., 2013). Cellulose, one of the main components in lignocellulose, can be converted into fermentable saccharides and fermented into ethanol by applying chemical or biological processes (Abdullah et al., 2014).

Given the complex structure of cellulose combined with hemicellulose and the fact that lignin restricts its contact with reaction media or enzymes, converting lignocellulosic biomass into saccharides or other chemicals requires a pretreatment or hydrolysis process to overcome its high resistance to dissolution and hydrolysis (Li et al., 2014; Xiao et al., 2014). Among many options, hydrothermal treatment by using supercritical or subcritical water has gained momentum as a promising process (Kruse, 2008). Benefitting from the high dissolving ability of hot compressed water and catalysis of ionized H^+, hydrothermal treatment offers the major advantages of rapid reaction, no chemical reagents, and efficient cost in lignocellulosic conversion (Xiao et al., 2014). Hydrothermal processes have been widely studied for lignocellulosic pretreatment (Zhao et al., 2009a), cellulose hydrolysis (Tolonen et al., 2013), and fractionation for biorefineries from

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lignocellulose (Gullon et al., 2012). Several studies have also presented hydrothermal technologies for lignocellulosic liquefaction, gasification, and carbonization (Resende et al., 2007; Funke and Ziegler, 2010; Tymchyshyn and Xu, 2010; Hoekman et al., 2011).

Several researchers previously reported the hydrothermal dissolution and hydrolysis of lignocelluloses with relatively high temperatures, especially with the involvement of supercritical water (above 374 °C and 22.1 MPa) and subcritical water (normally above 300 °C and 10 MPa) (Lü and Saka, 2012; Zhao et al., 2012). However, many of them found that monosaccharides decompose rapidly into unfermentable products during cellulose dissolution and hydrolysis, resulting in the loss of fermentable sugars (Kumar and Gupta, 2008; Zhao et al., 2015). This result is mainly attributed to the synchronous dissolution and hydrolysis of cellulose, especially in the conventional batch- or flow-type hydrothermal process for lignocellulosic conversion (Zhao et al., 2012). Moreover, synchronous dissolution and hydrolysis of lignocellulose at high temperatures result in the formation of various intermediates, such as phenolic and furfural, which are derived from hemicellulose and lignin degradation and inhibit cellulose hydrolysis or subsequent yeast fermentation (Qing et al., 2010; Kont et al., 2013).

To avoid the disadvantages caused by product degradation, considerable attention has been devoted to the reaction mechanisms of lignocellulosic dissolution and hydrolysis during hydrothermal treatment. According to previous studies, the decomposition of lignin, hemicellulose, and cellulose can be characterized by temperature as follows: hemicellulose mainly decomposes between 200 °C and 400 °C, cellulose decomposes at high temperatures of 300–400 °C, and lignin gradually decomposes between 180 °C and 600 °C (Libra et al., 2011). Several researchers reported that all hemicellulose, 35–60% of lignin, and 4–22% of cellulose can be dissolved with flow-type hydrothermal treatment at 200–230 °C, 34.5 MPa, and 15 min (Mosier et al., 2005). Therefore, different treatment temperatures can be utilized for hemicellulose and cellulose hydrolysis separately, given that cellulose is more resistant to hydrolysis than hemicellulose (Lü et al., 2009). The multi-step hydrothermal process has been applied to convert biomass waste, such as rapeseed straw, and depolymerization of hemicellulose, cellulose, and lignin has been implemented with a batch system at 210 °C, 270 °C, and 330 °C, respectively (Pinkowska and Wolak, 2013). Lü and Saka also reported that the semi-flow hydrothermal system, which is superior to the batch system in the respect of total saccharide production, provides the maximum saccharides from hemicellulose and cellulose in Japanese beech at 230 °C and 270 °C, respectively (Lü and Saka, 2010). However, clear fundamental understanding of the process, especially multi-level dissolution and hydrolysis with the semi-flow process, remains lacking (Kumar et al., 2010). In addition, no standard process conditions exist; as a result, each raw material should be individually studied and optimized (Rostagno et al., 2015).

To overcome the problem in the synchronous dissolution and hydrolysis of lignocellulosic compounds, a semi-flow reaction system was applied in this study to implement a multi-level hydrothermal process for lignocellulosic conversion. The semi-flow system keeps the undissolved materials in the dissolution unit as stationary phase and discharges the dissolved compounds from the system as mobile phase. This system structure offers different residence times to undissolved and dissolved compounds and thus avoids their insufficient dissolution and excessive degradation, respectively. Furthermore, the multi-level operation benefits the dissolution or hydrolysis of the major compounds in their respective optimal conditions. To examine the mechanisms of asynchronous dissolution and hydrolysis of lignin, hemicellulose, and cellulose, multi-level hydrothermal conversion of corn stalks was investigated with the semi-flow system in this study from the perspectives of chemical structure and component analysis. The variation in crystallinities, chemical bonds, compositions, and hydrolysates of lignocellulose was revealed with different hydrothermal conditions to enhance the understanding of hydrothermal lignocellulosic conversion and reveal the promising application of the multi-level semi-flow system to the recovery of valuables from lignocellulosic waste.

2. Materials and methods

2.1. Raw materials and chemicals

Corn stalks, which were obtained from farms in the suburbs of Beijing, China, were utilized as lignocellulosic substrate. The corn stalks were mechanically crushed into powder and sieved with a 0.63 mm sieve prior to the experiments.

The standard substances for high-performance liquid chromatography (HPLC) analysis, including cellopentaose, cellotetraose, cellotriose, and erythrose, were purchased from Toronto Research Chemicals Inc. (Canada). The other standard substances, such as cellobiose, glucose, xylose, fructose, glyceraldehyde, 1,6-anhydroglucose, and 5-HMF, were provided by Sigma–Aldrich Inc. (MO, USA).

2.2. Experimental apparatus and designs

A semi-flow hydrothermal reaction system was specially designed and manufactured for the sequential dissolution and hydrolysis of lignocellulosic materials. A diagram of the apparatus is shown in Fig. 1. The entire system is made of 316L stainless steel, and its different units are connected by pipelines with a diameter of 32 mm. Initially, a certain amount of raw materials in powder was loaded as solid phase in the dissolution unit, which was then sealed with the upstream and downstream pipelines. Subsequently, distilled water as liquid phase was pumped into the preheating unit and heated to a set temperature and then sent to the dissolution unit to dissolve the lignocellulosic materials. For first-stage dissolution, the dissolved materials flowed with the liquid phase into the termination unit to stop the reaction by water cooling. Meanwhile, the undissolved materials remained in the dissolution unit for further reaction until a set retention time. For the purpose of combining dissolution and hydrolysis experiments, after first-stage dissolution, the dissolution unit was shifted to a high temperature for second-stage dissolution. The liquid phase carrying dissolved materials flowed into the hydrolysis unit to hydrolyze the substances into small fractions, such as monosaccharides. After the entire process, the solid residues and liquid hydrolysates were collected and further analyzed.

Before each round of experiments, 7.0 ± 0.7 g of raw materials were loaded in the dissolution unit. The pressures of the dissolution unit were maintained at 4.5 ± 0.5 MPa for all the experimental rounds. The solid retention times for undissolved materials in the first- and second-stage dissolution were both 30 min, and the hydraulic retention times for liquid phase in both stages were 6 min. The temperatures for the different experimental strategies are listed in Table 1. The temperature of the hydrolysis unit was maintained at 280 °C according to our previous work on oligosaccharide hydrolysis (Zhao et al., 2009a). Two parallel experiments were performed for all the experimental conditions, and the residual samples collected from the parallel experiments were mixed for analysis purpose.