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Optimization of supercritical phase and combined supercritical/subcritical conversion of lignocellulose for hexose production by using a flow reaction system

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ABSTRACT

A flow reaction system was utilized to investigate lignocellulose conversion using combined supercritical/subcritical conditions for hexose production. Initially, investigation of cellulose hydrolysis in supercritical water and optimization of reaction parameters were done. Oligosaccharide yields reached over 30% at cellulose concentrations of 3–5 g L^{-1} and reaction times of 6–10 s at 375 °C, and 2.5–4 g L^{-1} and 8–10 s at 380 °C. Temperatures above 380 °C were not appropriate for the supercritical phase in the combined process. Subsequently, conversion of lignocellulosic materials under combined supercritical/subcritical conditions was studied. Around 30% hexose was produced from corn stalks under the optimal parameters for supercritical (380 °C, 23–24 MPa, 9–10 s) and subcritical (240 °C, 8–9 MPa, 45–50 s) phases. Flow systems utilizing the combined supercritical/subcritical technology present a promising method for lignocellulosic conversion. The results of this study provide an important guide for the operational optimization and practical application of the proposed system.

1. Introduction

Considering the rapid decrease in petroleum reserves worldwide, the development of practical methods for transforming biomass into biofuels, such as ethanol and other chemicals, to supplement or gradually replace fossil fuels is becoming increasingly important (Sun et al., 2009). Cellulose, the basic component of plants and lignocellulosic wastes, is the most abundant and renewable biomass resource in nature. Cellulose in lignocellulose can be converted to ethanol by fermentation but only after chemical or physical pretreatment followed by hydrolysis (Rostrup-Nielsen, 2005). Pretreatment and hydrolysis technologies have been recognized as key processes for producing bioethanol from cellulose, and many technologies, including acid treatment, steam explosion, and enzymatic hydrolysis, have been developed and investigated (Galbe and Zacchi, 2007; Ruffell et al., 2010; Sun and Cheng, 2005; Taherzadeh and Karimi, 2008).

Hydrothermal technology has recently attracted increased attention due to its high efficiency in lignocellulose conversion (Boussarsar et al., 2009; Díaz et al., 2010; Saka, 2006). Many researchers have reported the successful dissolution and hydrolysis of cellulose and lignocelluloses through hydrothermal methods, including those involving supercritical water and subcritical water (Kumar et al., 2010; Lu et al., 2009; Matsunaga et al., 2008; Nakata et al., 2006; Zhuang et al., 2009). Cellulose can be hydrolyzed first into oligosaccharides, including cellopentaose, cellotetraose, cellotriose, and cellobiose, and then into hexoses, including glucose and fructose, which can be further decomposed into non-fermentable components. Considering the high dissolution rate of polymers in supercritical water and the low decomposition rate of fermentable sugars in subcritical water, a combined supercritical and subcritical process has been suggested and investigated. In such a process, cellulose is pretreated and hydrolyzed to produce oligosaccharides in supercritical water, followed by secondary hydrolysis in subcritical water to convert oligosaccharides into fermentable hexoses (Ehara and Saka, 2005; Zhao et al., 2009b).

In our previous work, important academic and experimental results relevant to the efficiency of and operational conditions for producing fermentable hexoses from cellulose, corn stalks, and wheat straw using a batch reaction system were generated (Zhao et al., 2009a,b,c). Considering the non-continuity and high-energy cost of the batch system, a flow-type reaction system was designed and proven feasible for combined supercritical and subcritical water treatment (Zhao et al., 2011). Optimum supercritical conditions, which influence oligosaccharide yields in a combined process, are crucial to hexose production. Moreover, collection of intermediate products from the supercritical phase is difficult when performing combined experiments in a flow reactor. Therefore, the current work first focuses on the supercritical phase to determine optimum supercritical conditions for the combined supercritical/subcritical treatment and then investigates for the

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first time the combined supercritical and subcritical conversion of natural lignocellulosic materials using a flow reaction system.

2. Methods

2.1. Flow reactor for cellulose and lignocellulose treatment with supercritical and subcritical water

The hydrolysis of cellulose in supercritical water was carried out in a flow reaction system for the combined process, that was described elsewhere (Zhao et al., 2011). This system consisted of a water tank and pump, material slurry tank and pump, preheater, supercritical phase, primary cooler, subcritical phase, final cooler, and product collectorn (Fig. 1). The preheater was composed of a coil pipe at the interior and a salt bath filled with 1:1 w/w of $NaNO_3$ and KNO_3 at the exterior, which provided an operating temperature of 260–500 °C. The supercritical phase included a supercritical reactor on the inside (ϕ = 4 mm, l = 800 mm, V = 10 mL), and a salt bath heater on the outside (similar information with that of the preheater). The subcritical reaction system includes a subcritical reactor (ϕ = 7 mm, l = 1300 mm, V = 50 mL) with an electric heater outside (providing a temperature of 100–350 °C). The supercritical reactor could be replaced with similar reactors of different lengths to accommodate different volumes during actual operation. Especially, the system had a tube that directly connected the primary and final coolers; this setup allowed supercritical reactions to be carried out separately, without involving the subcritical phase when necessary.

The flow reaction system used tubes made of stainless steel 316 (ϕ = 4 mm) for circulation. During the supercritical process, deionized water from the water tank was pumped into the preheater (preheated to a chosen temperature to shorten the heating time of the materials) and then mixed with the material slurry pumped from the material slurry tank. The materials were rapidly heated up and the mixture was immediately transferred into the supercritical phase. The product of the reaction in the supercritical water was cooled by the primary cooler to stop the reaction at the supercritical stage and then directly collected by the product collector. During the combined supercritical and subcritical process, the product from the supercritical reactor was brought to the subcritical reactor and then cooled and collected by the final cooler and product collector, respectively. Temperatures in the preheater and supercritical and subcritical reactors were controlled by a temperature control system using thermoelements. Reaction time was considered as the residence time of the mixture in the reactors (i.e., the time it took for the mixture to flow through the reactors). Pressures inside the reactors were measured by manometers and adjusted by reducing valves.

2.2. Chemicals and analysis

Microcrystalline cellulose powder (purity >99.9%, Beijing Fengli Jingqiu Commerce and Trade Co., Ltd.) was used as the substrate for supercritical hydrolysis. Corn stalks obtained from farms in the suburbs of Beijing, China, served as natural lignocellulosic materials for conversion under combined conditions. To achieve sufficient contact between lignocellulose and supercritical/subcritical water, corn stalks were mechanically crushed into powders and sieved through a 40 mesh sieve.

Cellulose in corn stalks was measured by anthrone colorimetry after hydrolysis with concentrated sulfuric acid. Hemicellulose was measured by orcinol colorimetry after hydrolysis with hydrochloric acid. Lignin was measured by ashing after hydrolysis with concentrated sulfuric acid.

High performance liquid chromatography (HPLC, Shimadzu, LC-10ADvp, RID-10A, Japan) was performed to quantify the compounds in the liquid hydrolysis products, including cellopentaose, cellotetraose, cellotriose, cellobiose, glucose, xylose, fructose, erythrose, glyceraldehyde, 1,6-anhydroglucose, dihydroxyacetone and 5-HMF. Standard substances of HPLC grade were purchased from Sigma–Aldrich Inc. (MO, USA). Analysis was conducted using a sugar column (Shodex, Sugar KS-801, Japan) at 50 °C, 1.0 mL min^{-1}, and 3.0 MPa. Oligosaccharide yield was calculated from the cellopentaose, cellotetraose, cellotriose, and cellobiose yields; hexose yield was calculated by summation of the glucose and fructose yields.

2.3. Experimental design and data analysis

This study first focused on cellulose conversion in the supercritical phase and then on conversion of corn stalks under combined supercritical and subcritical conditions. Initially, 60 g of cellulose and 6 L of deionized water were mixed in the material slurry tank; the water tank was filled with deionized water. In the flow reaction

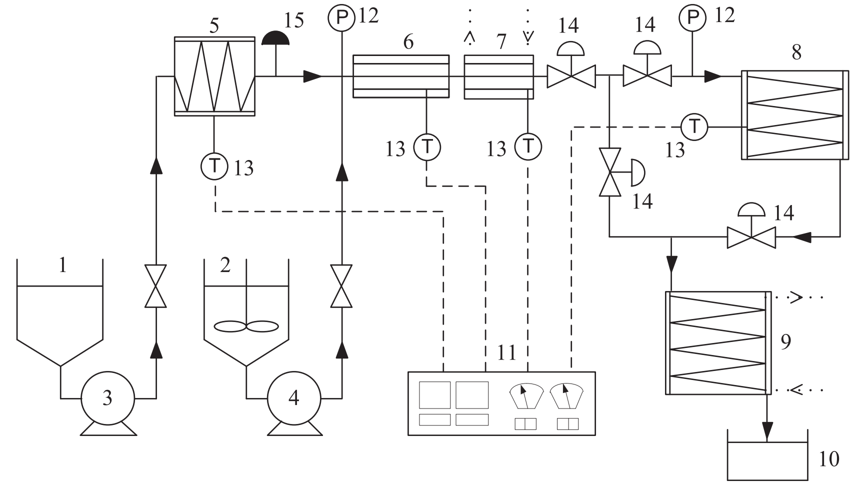

Fig. 1. Flow reaction system for the combined supercritical/subcritical process of lignocellulosic conversion. (1) Water tank, (2) material sludge tank, (3) water pump, (4) material sludge pump, (5) preheater, (6) supercritical reactor, (7) primary water cooler, (8) subcritical reactor, (9) final water cooler, (10) product collector, (11) temperature control system, (12) manometer, (13) thermoelement, (14) reducing valve, (15) safety valve.