



Supercritical hydrolysis of cellulose for oligosaccharide production in combined technology

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ABSTRACT

A combined supercritical/subcritical technology was used as a pre-treatment and hydrolysis method for ethanol production from cellulose/lignocelluloses. In a batch study for supercritical hydrolysis, which is the primary step of the combined technology, 60 mg of microcrystalline cellulose in 2.5 ml deionized water was loaded into each reactor and heated in a salt bath at a selected temperature for a specified reaction time. Cellulose was quickly hydrolyzed to oligosaccharides, hexoses and other small molecular products at temperatures above the critical point of water. Temperature and reaction time were the two key parameters that determined the products of cellulose hydrolysis. The highest yield of oligosaccharides (approximately 40%) was obtained at optimum conditions of 380 °C and a reaction time of 16 s. The corresponding yield of hexoses was 24%, giving a maximum yield of hydrolysis products of approximately 63%. A complete decomposition of hydrolysis products occurred at higher temperatures and/or longer reaction times. A kinetic analysis was performed to explain the reaction of cellulose in supercritical water. The results presented here provide a rigid framework for the use of combined supercritical/subcritical technology in subsequent research.

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1. Introduction

Lignocellulosic waste, such as corn stalks, is a potential biofuel source. Ethanol production technology, the typical resource technology for lignocellulosic waste, has received much attention due to its feasibility and valuable products. However, bottlenecks still remain in the efficient conversion of lignocellulose into ethanol. Firstly, it is difficult to hydrolyze cellulose due to its large molecular structure, which imparts crystallinity and poor solubility. Secondly, the presence of lignin around the cellulose fibers prevents direct contact between cellulose and hydrolyzing solvents. To address these hurdles, many technologies have been developed for the pre-treatment and hydrolysis of lignocelluloses, including such technologies as acid treatment, steam explosion and enzymatic hydrolysis [1–3]. In addition to these approaches, subcritical and supercritical water treatments have also been investigated and have shown some particular advantages, such as high reaction rate, no catalyst requirement and no product inhibition.

There is only limited information available regarding the mechanism of cellulose hydrolysis in supercritical and subcritical water [4–6]. For example, Sasaki et al. examined the hydrolysis of cellulose and oligosaccharides in supercritical water, and found that cellulose

can initially be converted into water-soluble oligosaccharides including cellobiose, cellotriose, cellotetraose and cellopentaose. Thereafter, the original cellulose was converted to glucose, fructose and assorted dehydration and fragmentation products [7,8]. Fig. 1 shows the reaction mechanism of cellulose hydrolysis in supercritical water. The pre-treatment of lignocelluloses in supercritical water is dependent on the high capacity of supercritical water for dissolution and catalysis, which allows separation of the lignin from cellulose and rapid hydrolysis of cellulose with the catalysis of H⁺ ionized [9]. However, Bonn et al. reported that cellulose hydrolysis in supercritical water can produce a high yield of oligosaccharides, but at the same time a high yield of glucose fragmentation products, which are inhibitors of fermentation [10]. This may be attributed to the fact that glucose generated from cellulose decomposes rapidly, being converted into erythrose, furfural and other unfermentable products [11,12]. In this sense, supercritical technology for lignocellulose conversion cannot result in a satisfactory yield of fermentable sugars.

Nonetheless, several research studies on cellulose conversion in subcritical water have indicated that the decomposition rate of glucose decreases rapidly with the decreases in reaction temperature and pressure. For instance, the decomposition rate of glucose at 400 °C is several hundred times greater than the rate at 300 °C [10]. The subcritical temperature of water can lead to higher density, and subcritical water is reported to be more efficient in producing glucose than is supercritical water [13]. Jin et al. found that cellulose

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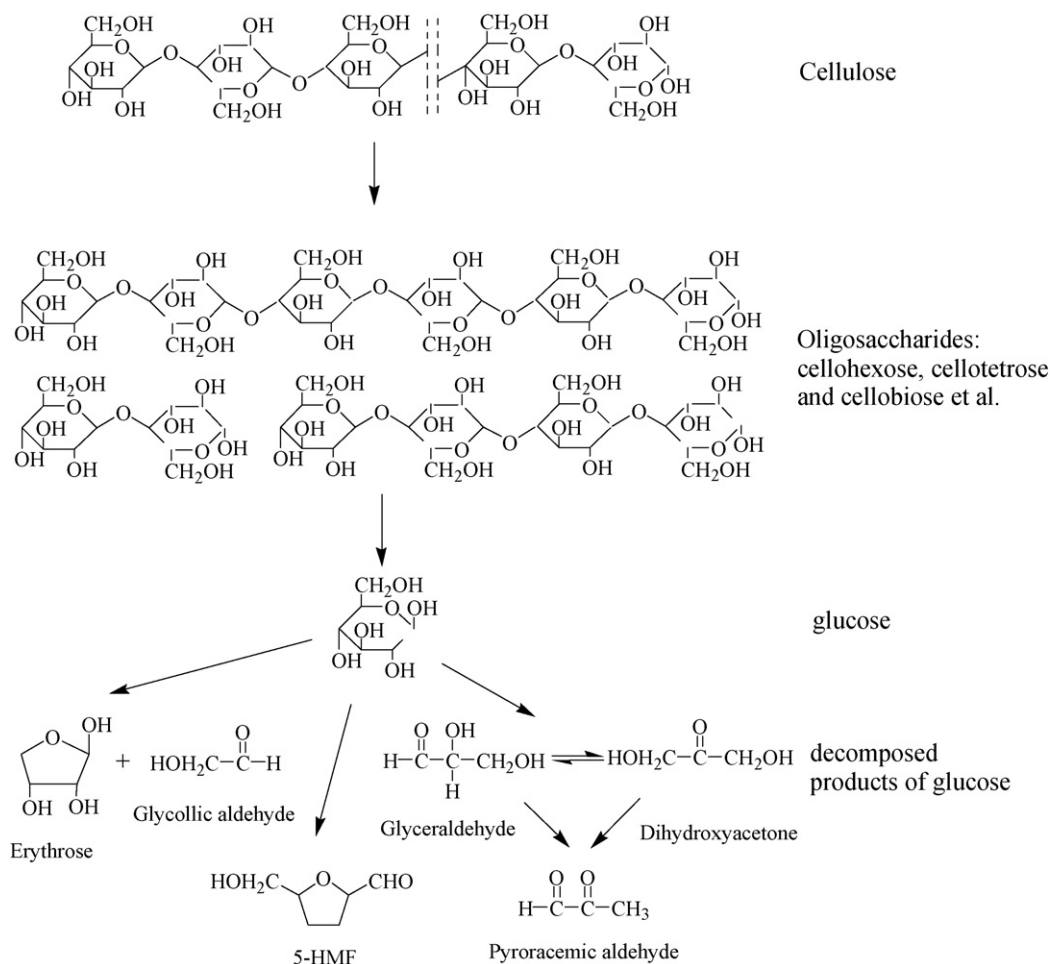


Fig. 1. Reaction mechanism of cellulose hydrolysis in supercritical water.

hydrolyzes into glucose in 2 min at 300 °C and 8.9 MPa, but that the glucose decomposes in 30 s under the same conditions. This suggests that the hydrolysis rate of cellulose in subcritical water is much slower than the rate of glucose decomposition, making it difficult to obtain a high yield of fermentable sugars [14]. Furthermore, the pre-treatment of lignocelluloses in subcritical water shows an unsatisfactory efficiency due to the difficulty in separating lignin from the cellulose. These explain why fermentable sugars are difficult to produce from lignocellulose at subcritical conditions.

To overcome the issues mentioned above, a combined supercritical/subcritical technology has been proposed for lignocellulose pre-treatment and hydrolysis. There are two major approaches involved this method. First, the lignocelluloses are pre-treated and hydrolyzed in supercritical water to remove the lignin and to produce oligosaccharides from cellulose. Subsequently, the oligosaccharides are hydrolyzed into hexoses in subcritical water to produce predominantly glucose and fructose. This method can simultaneously obtain a high yield of fermentable sugars in an efficient manner and prevent the further decomposition of glucose into undesirable products [15]. Ehara et al. performed a flow-type combined supercritical/subcritical experiment under at 400 °C, 40 MPa for 0.1 s followed by 280 °C, 40 MPa for 15–45 s. The highest yield of glucose was 29.2%. In contrast, a separate supercritical experiment (400 °C, 40 MPa, 0.1–0.3 s) resulted in only 10.5% glucose [16].

However, there are still many unresolved problems in supercritical/subcritical cellulose hydrolysis, such as optimization of reaction conditions to enhance yields of targeted products, as well as scientific questions regarding the basic kinetics of cellulose thermal

hydrolysis. Given its potential, and notwithstanding its still to be resolved problems, further research is desirable. The purpose of this paper was therefore to optimize conditions for generation of oligosaccharides from cellulose in supercritical water, as a prelude to the development of a combined supercritical/subcritical technology for production of high yields of fermentable sugars. The effects of reaction temperature and time on cellulose hydrolysis in supercritical water were therefore investigated in detail, over a temperature range of 374–386 °C and time intervals of 14–24 s. The yields of the fractionated portions of cellulose, especially those of oligosaccharides (including cellobiose, cellotriose, cellotetraose and cellopentaose) and hexoses (including glucose and fructose), were then analyzed and compared. A kinetic analysis for cellulose hydrolysis in supercritical water was performed as well.

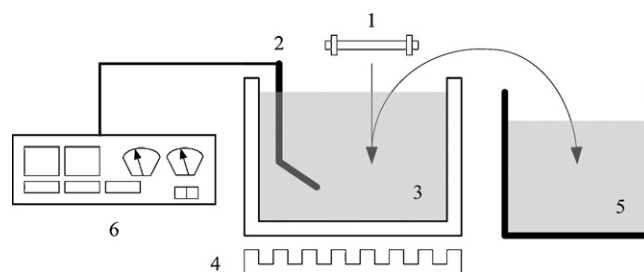


Fig. 2. Batch system of hydrothermal reaction (1) Reactor; (2) Thermolement; (3) Salt bath; (4) Electric stove; (5) Water cooler; (6) Temperature control system.

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