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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.

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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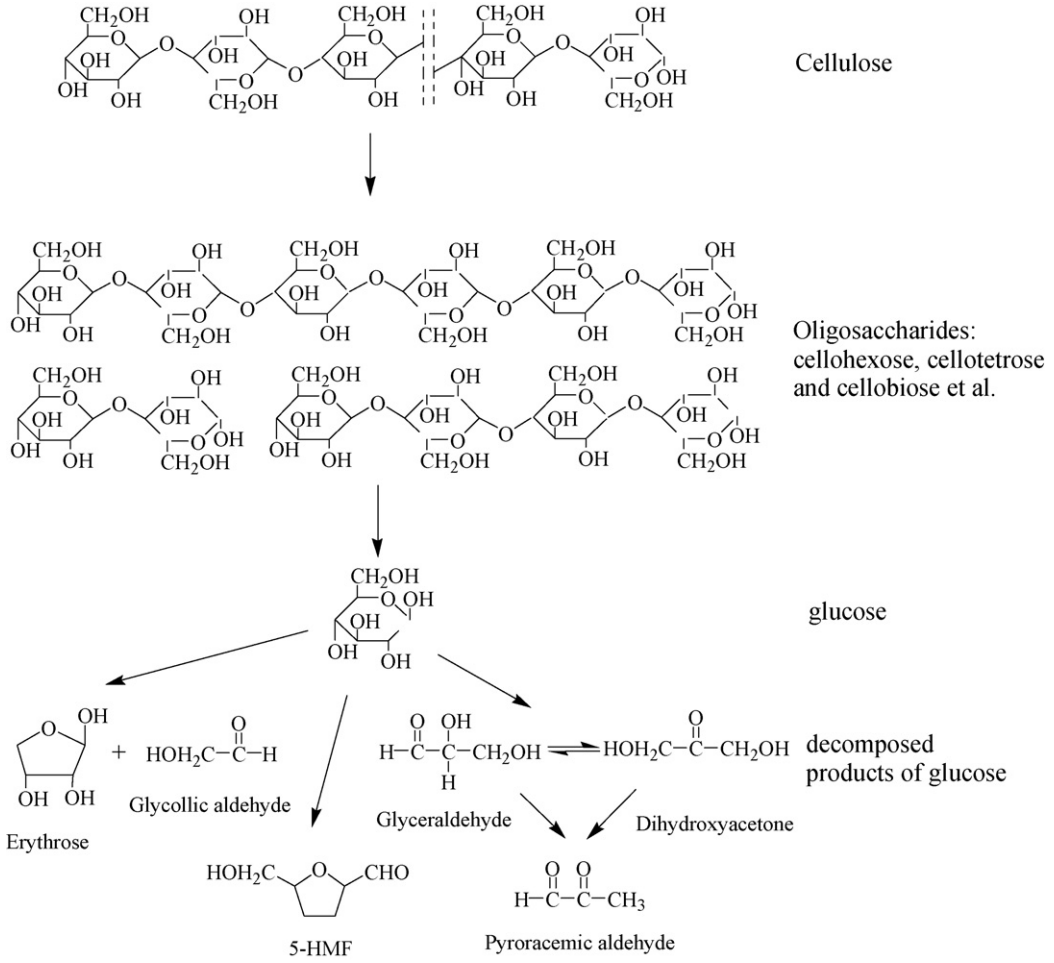

Fig. 1. Reaction mechanism of cellulose hydrolysis in supercritical water.

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.

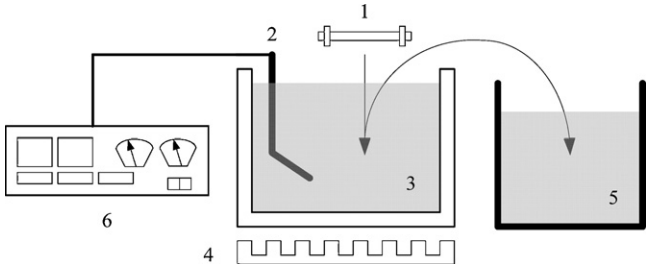

Fig. 2. Batch system of hydrothermal reaction (1) Reactor; (2) Thermoelement; (3) Salt bath; (4) Electric stove; (5) Water cooler; (6) Temperature control system.

2. Materials and methods

2.1. Samples and chemicals

Microcrystalline cellulose (Beijing Fengli Jingqiu Commerce and Trade Co., Ltd.) was used as the cellulosic substrate for hydrolysis. High performance liquid chromatography (HPLC) grade chemicals, including cellobiose, cellotriose, cellotetraose, cellopentaose, glucose and fructose, were obtained from Sigma–Aldrich Inc.

2.2. Supercritical treatment system

The supercritical treatment and hydrolysis experiments, which have been reported in a previous paper [15], were conducted in the batch reactor system illustrated in Fig. 2. The system consists of reactors, a temperature controller, a salt bath and a water cooler. The reactor was made of stainless steel 316 tubing (7 mm inner diameter, 2.5 mm wall thickness and 130 mm length) with two sealing screw-caps, providing an inner volume of 5 cm^3. During the experiments, two parallel reactors, loaded with desired amount of test material and deionized water, were immersed horizontally into the salt bath that had been preheated to the chosen temperature. The reactors were shaken to enhance mixing and heat transfer during the reaction. After the end of the desired reaction time, the reactors were removed from the salt bath and immediately placed into the water cooler to stop the reaction. Reaction time is defined as the time that the reactor was kept in the salt bath. Since the time required to raise the temperature of the reaction medium from 20 to 380 °C was about 15 s, the real reaction time was shorter than the apparent reaction time. Reaction pressures inside the reactor were calculated according to the equation of temperature, density and pressure.

2.3. Chemical analysis

An elemental analyzer (CE-440) was utilized to measure the total carbon percentage in the raw materials. The liquid samples remaining after the reactions were analyzed by total organic carbon analyzer (Shimadzu, TOC-5000) and by HPLC (Shimadzu, LC-10ADvp, RID-10A) equipped with a sugar column (Shodex, Sugar KS-801). Given that, in most cases, the carbon balance evaluated by TOC was above 95%, gas analysis was not conducted. The fractions in the liquid samples were quantified for cellobiose, cellotriose, cellotetraose and cellopentaose content, as these are the soluble hydrolysis products of cellulose, as well as for glucose, fructose, erythrose, glyceraldehyde, 1,6-anhydroglucose, dihydroxyacetone and 5-hydroxymethyl-2-furfural (5-HMF) content, as these are the hydrolysis or decomposition products of oligosaccharides.

3. Results

3.1. Effect of temperature on cellulose solubilization and hydrolysis

In the batch study, 60 mg of microcrystalline cellulose in 2.5 ml deionized water was loaded into each reactor, and was reacted under the conditions mentioned above after the reactor was sealed. The time for maximum solubilization of the cellulose substrate was negatively correlated with the reaction temperature; that is, the higher the temperature, the shorter the reaction time. Cellulose was completely liquefied above 380 °C, whereas it was only partially liquefied at temperatures lower than 378 °C and after reaction times shorter than 20 s. However, as seen in Fig. 3, a different trend was observed for sugar production from cellulose hydrolysis, in that the highest yield of hydrolysis products (oligosaccharides and hexoses)

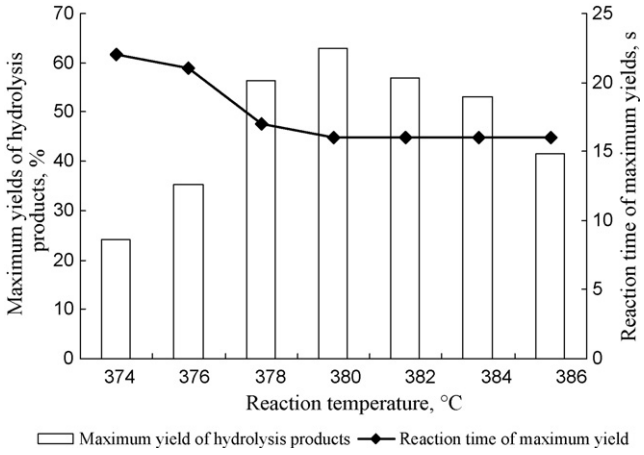

Fig. 3. Variation of maximum sugar percents at different temperatures.

was obtained at 380 °C and this decreased as the temperature was increased.

Fig. 4 shows the effect of temperature on hydrolysis products and indicates that approximately 50% of cellulose was hydrolyzed into oligosaccharides and hexoses in 16 s at the temperature of 378 °C, with respective yields of 24.9% and 7.5%. Cellulose hydrolysis was consistently accompanied by the decomposition of glucose as the temperature rose. At 380 °C, approximately 80% of the cellulose was hydrolyzed, and the yields of oligosaccharides and hexoses were much higher than those at 378 °C, reaching 38.9% and 24.0%, respectively. Only a small portion was converted into pyrolysis products. In contrast, at 382 °C, oligosaccharide production was reduced by 15.1% of the levels seen at 380 °C but 9.2% more hexoses were detected, which was suggestive of a rapid decrease in hydrolysis products due to pyrolysis at higher temperature. Therefore, it is difficult to obtain a high yield of fermentable sugars at higher temperature due to the accompanying accelerated decomposition of the hydrolysis products.

Sasaki reported that the hydrolysis rate of cellulose increases drastically above the critical point and becomes more rapid than the dissolution rate of glucose. Hence, this results in a higher yield of oligosaccharides than of glucose [8]. However, the reaction rate constants of cellulose and oligosaccharide hydrolysis and the decomposition of glucose become much larger with an increase in temperature. In this sense, a temperature just slightly above the critical point of water can be adopted to produce oligosaccharides under controllable reaction conditions [17].

3.2. Effect of reaction time on cellulose and oligosaccharide hydrolysis

Fig. 5 shows the curve of liquefaction ratio of cellulose with reaction time at 380 °C, the optimal temperature determined above, and indicates that cellulose is not dissolved and liquefied in the batch reactors when the reaction time is shorter than 14 s, and that the liquefaction ratio is only around 60% at 15 s. On the other hand, the liquefaction ratio increased alongside the reaction time, increasing to as much as 80% at 16 s and up to 95% for more prolonged reaction times.

Fig. 6 shows typical HPLC chromatograms of the products obtained with different reaction times. Oligosaccharides can be detected in a short time and the concentrations of glucose and other small molecular substances are very low. As the duration of the reaction time is extended, the concentration of oligosaccharides reaches a maximum at around 16 s and then decreases gradually. Glucose increases continuously before 17 s from 12.6% to 24.0%, but thereafter begins to decrease due to the high rate of decomposition,

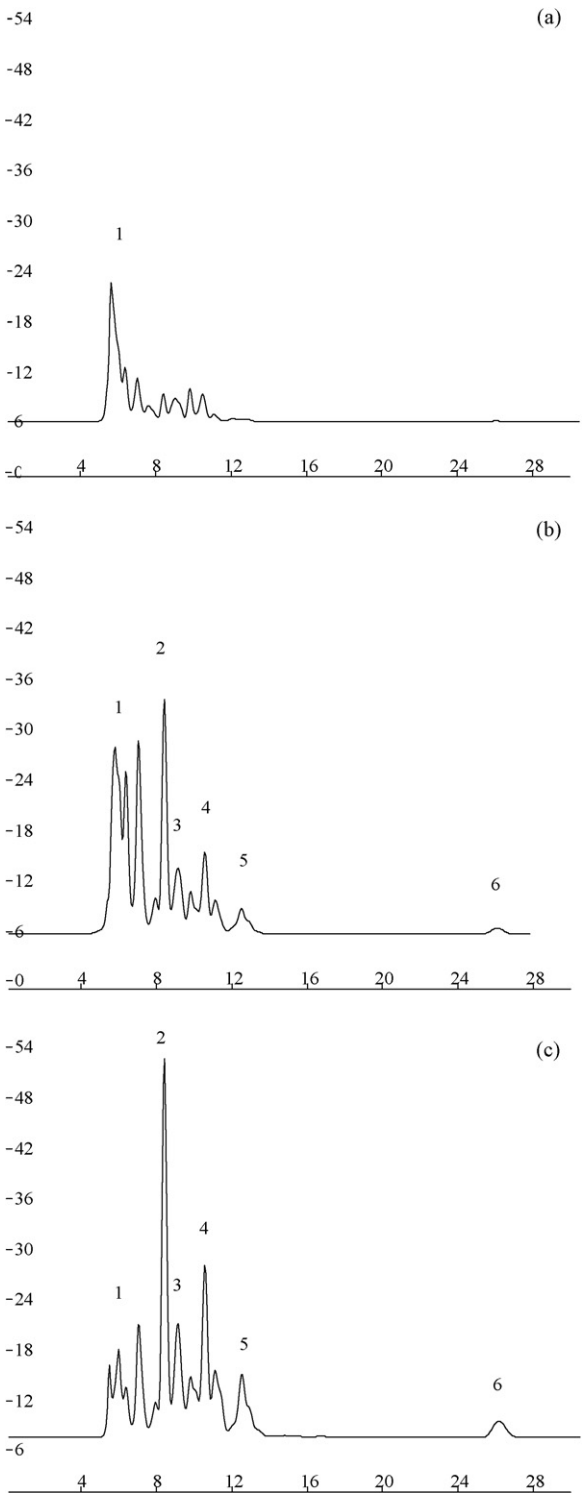

Fig. 4. Chromatograms of products in different reaction temperatures (reaction times are all 16 s) (a) 378 °C; (b) 380 °C; (c) 382 °C. 1. Oligosaccharides (from left to right: cellopentaose, cellotetraose, cellotriose, cellobiose; 2. Glucose; 3. Fructose; 4. Erythrose; 5. 1,6-Anhydroglucose; 6. 5-HMF.

indicated by the increasing yield of its fragmentation products, such as dihydroxyacetone and 5-HMF.

Fig. 7 shows the yields of hexoses after 18 s at different temperatures, and indicates that hexoses decompose rapidly with the extension of reaction time, and are eventually converted to fragmentation products. The rate of hexose decomposition increases

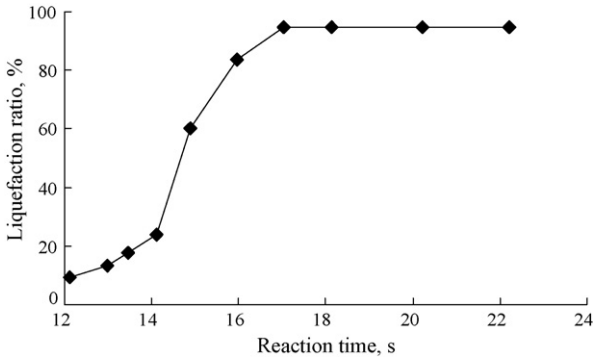

Fig. 5. Curve of liquefaction ratio of cellulose with reaction time at 380 °C.

with increases in reaction temperature. Therefore, a higher yield of oligosaccharides can be obtained with a relatively short reaction time. Likewise, a better hydrolysis efficiency of cellulose results when the temperature is slightly above the critical point of water.

We were able to demonstrate that the hydrolysis rate of oligosaccharides is lower than the decomposition rate of hexoses in supercritical water. This accounts for the difficulty in generating levels of glucose from cellulose. However, it is feasible to generate a substantial accumulation of oligosaccharides in a short reaction time under supercritical condition because the hydrolysis rate of cellulose is higher than that of oligosaccharides.

3.3. Optimum condition of oligosaccharides generation from cellulose

A further study of the optimum condition of cellulose hydrolysis to oligosaccharides was conducted at around 380 °C and 16 s. This is in reference to the results of the abovementioned analysis. The results are shown in Table 1.

As seen in Table 1, the subtotal showing yields of oligosaccharides increases to a maximum and then decreases, both when the temperature increases and as reaction time is extended. For instance, at 380 °C, a higher yield of cellopentaose resulted as a consequence of a shorter reaction time, in accordance with the reaction mechanism of cellulose hydrolysis. At the same time, cellotetraose, cellotriose and cellobiose were produced and were all directly hydrolyzed to glucose. Therefore, oligosaccharides can be considered as the primary hydrolysis products in the whole process. Secondary hydrolysis products included glucose and fructose, an isomerization product of glucose. In this series of experiments, the highest yield of oligosaccharides was 38.9%, obtained in 16 s at 380 °C, with a corresponding yield of 24.0% hexoses. The maximum yield of hexoses was 27.2% and was obtained under the reaction conditions of 378 °C and 17 s.

Table 1 also shows the decomposition products of oligosaccharides and hexoses. The main decomposition product was erythrose, which accounted for almost half of the yields of decomposition products and which increased continuously with extensions in reaction time. For example, the yield of erythrose was 9.1% at 16 s at 380 °C. The subtotal yield of fragmentation products was 20.7%. Glyceraldehyde, dihydroxyacetone, and 5-HMF showed a similar pattern of production trend to that seen for erythrose.

Under conditions of 380 °C and 16 s, which yielded the maximum amounts of oligosaccharides and low levels of decomposition products (20.7%), the subtotal yield of hydrolysis products (including oligosaccharides and hexoses) reached 62.9%. Hence, 380 °C and 16 s were considered as the optimum conditions for cellulose hydrolysis in supercritical water. These results can provide reliable evidence for the combined supercritical/subcritical technology in the subsequent research.

Table 1
Yields of products in water-soluble portions from cellulose treated in supercritical water.

Product compositions	Yield %											
	378 °C				380 °C				382 °C			
	15 s	16 s	17 s	18 s	15 s	16 s	17 s	18 s	15 s	16 s	17 s	18 s
Primary hydrolysis products												
Cellopentaose	13.6	15.1	3.8	5.1	16.9	16.2	4.3	3.5	16.6	6.5	5.7	4.0
Cellotetraose	3.9	5.1	5.9	7.0	5.8	4.5	8.0	10.7	5.1	3.0	6.9	6.3
Cellotriose	2.7	4.1	1.8	1.5	4.4	5.6	1.0	0.8	5.0	3.5	2.1	0.8
Cellobiose	4.7	8.0	8.0	4.8	7.8	12.6	2.2	1.0	10.5	10.8	8.4	2.9
Subtotal	24.9	32.3	19.5	18.4	34.9	38.9	15.5	16.0	37.3	23.8	23.1	14.0
Secondary hydrolysis products												
Glucose	3.8	8.8	27.2	22.1	7.2	16.8	13.7	10.6	12.2	24.6	20.0	19.0
Fructose	3.7	4.9	9.6	10.1	5.4	7.2	9.5	8.8	5.8	8.6	9.1	10.7
Subtotal	7.5	13.7	36.8	32.2	12.6	24.0	23.2	19.4	18.0	33.2	29.1	29.7
Sum of hydrolysis products	32.4	46.0	56.3	50.6	47.5	62.9	38.7	35.4	55.3	57.0	52.2	43.7
Fragmentation products of glucose												
Glyceraldehyde	0.0	0.1	1.8	1.8	0.0	0.0	3.2	6.2	0.3	0.9	1.3	2.6
Erythrose	2.8	4.4	17.5	20.0	4.0	9.1	23.5	24.4	6.6	11.8	14.5	18.7
1,6-Anhydroglucose	0.3	1.4	6.4	6.1	1.8	4.6	4.9	4.1	2.1	5.1	5.2	5.9
Dihydroxyacetone	0.1	0.1	2.2	3.5	0.0	0.0	6.7	6.6	0.5	0.5	1.5	3.3
5-Hyroxymethyl-2-furfural	0.9	1.0	2.8	3.5	1.0	1.0	4.0	4.4	1.3	2.2	2.5	4.1
Others	10.0	9.9	6.2	6.6	6.0	6.0	13.5	13.6	12.2	12.5	17.3	16.2
Subtotal	14.1	16.9	36.9	41.5	12.8	20.7	55.8	59.3	23.0	30.5	42.3	50.8
Total	46.5	62.9	93.2	92.1	60.3	83.6	94.5	94.7	78.3	90.0	94.5	94.5

3.4. Kinetic analysis of cellulose hydrolysis in supercritical water

Based on the results of cellulose hydrolysis in supercritical water, a kinetic analysis was performed. The mechanism of cellulose hydrolysis (Fig. 1) can be simplified according to the consecutive reaction course below, in which k_1, k_2, k_3 are the reaction rate constants of cellulose hydrolysis, oligosaccharide hydrolysis and hexose decomposition, respectively.

$$\text{Cellulose(A)} \xrightarrow{k_1} \text{Oligosaccharides(B)} \xrightarrow{k_2} \text{Hexoses(C)} \xrightarrow{k_3} \text{Others(D)} \quad (1)$$

The reaction rate equations of the three steps are shown as follows:

$$\frac{dC_A}{dt} = -k_1 C_A \quad (2)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (3)$$

$$\frac{dC_C}{dt} = k_2 C_B - k_3 C_C \quad (4)$$

C_A, C_B, C_C in the equations stand for the concentrations of cellulose, oligosaccharides and hexoses, which can be translated from the yields in Table 1. The linear and curve fittings were applied to calculate the reaction rate constants of the three steps. In Step A, for instance, Eq. (5) is the integral equation of Eq. (2) and can be expressed as Eq. (6), in which concentration of cellulose (C_A) is translated to conversion rate (X_A). Eq. (7), which was derived from Eq. (6), represents linear fitting. The results of fitting are shown in Fig. 8 and the slopes of the fitting lines indicate the reaction rate constants of each step.

$$C_A = C_{A,0} e^{-k_1 t} \quad (5)$$

$$X_A = e^{-k_1 t} \quad (6)$$

$$\ln\left(\frac{1}{X_A}\right) = k_1 t \quad (7)$$

Fig. 8 shows that the reaction rate constant of cellulose hydrolysis at 378 °C was 1.04 s^{-1}. This was much lower than 1.70 s^{-1} at 380 °C or 1.86 s^{-1} at 382 °C and is in accordance with the experimental results that showed that the liquefaction and hydrolysis of cellulose proceeded with difficulty at temperatures lower than 380 °C. Furthermore, the difference between the reaction rate constants of cellulose hydrolysis at 380 and 382 °C was not as significant as the difference between the constants at 378 and 380 °C. This explains the jump in cellulose dissolution and hydrolysis over the critical point (Fig. 3). The reaction rate constants for decomposition of oligosaccharides and hexoses can be calculated in a similar way. For instance, the former at 380 °C was 0.93 s^{-1} and the latter was 1.02 s^{-1}, indicating a higher reaction rate of hexose decomposition than of production. For this reason, it is difficult to accumulate large amounts of fermentable sugars under supercritical conditions. In contrast to the rate of cellulose hydrolysis, the rate of oligosaccharide decomposition is much lower; hence, it favors the accumulation of oligosaccharides. The kinetics analysis reveals the qualitative and quantitative relationships between the reaction rates of each of the steps of the cellulose hydrolysis reaction in supercritical water, and proves that a combined process is both promising and feasible.

4. Discussion

4.1. Investigation of optimum reaction conditions for cellulose hydrolysis in supercritical water

The overall efficiency of hydrolysis of cellulose to glucose in supercritical water is governed by many factors, such as cellulose solubility, oligosaccharide hydrolysis, and glucose decomposition. Ehara et al. reported a yield of oligosaccharides of 1.6% in a batch-type reactor under supercritical water condition (380 °C and 100 MPa) [13]. In their subsequent research with a flow-type reactor, a temperature of 400 °C was used and the maximum yield of oligosaccharides was 32.2%, with a corresponding hexoses yield of 14.5% [16]. The higher decomposition rate of hydrolysis products at higher temperature and pressure accounted for the low sugar production, which can be confirmed using the kinetic analysis of cellulose hydrolysis in the current paper. Moreover, more energy was also consumed under these conditions. Our system reported a higher yield of hydrolysis products (15% more) with lower energy requirements (380 °C and 22 MPa).

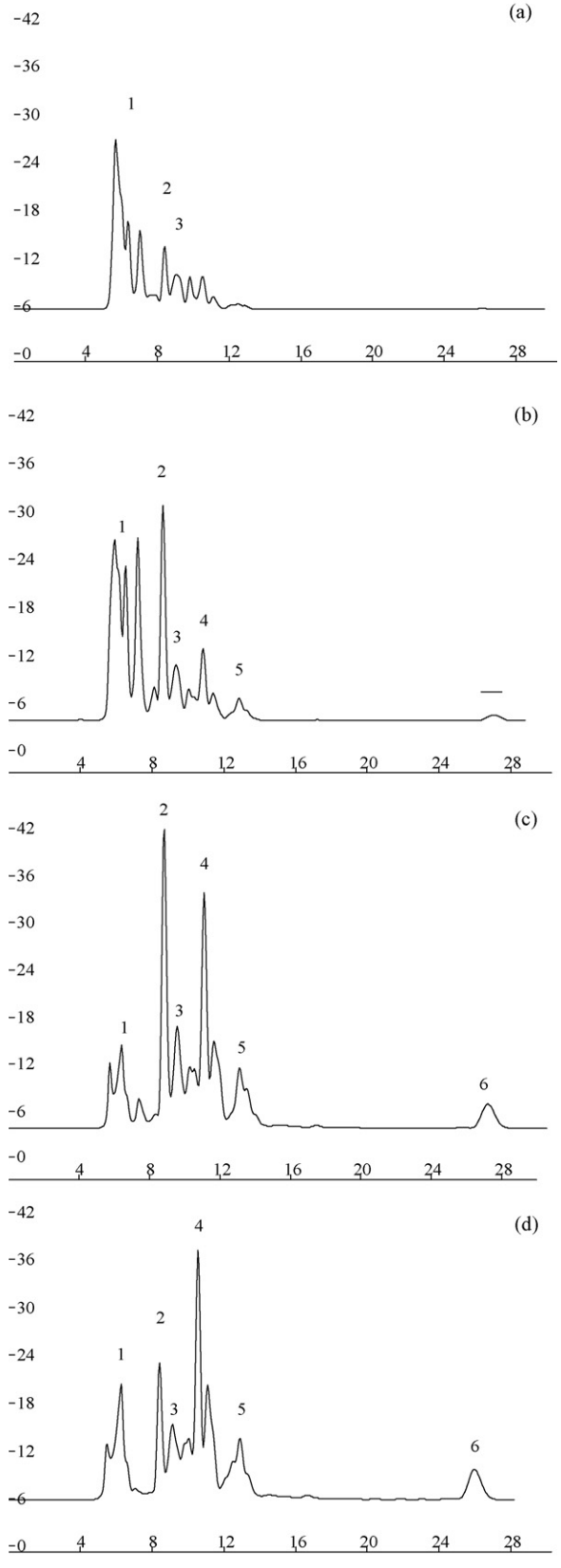

Fig. 6. Chromatograms of products at different reaction times (reaction temperatures are all 380 °C) (a)15 s; (b) 16 s; (c) 17 s; (d) 18 s. 1. Oligosaccharides (from left to right: cellopentaose, cellotetraose, cellotriose, cellobiose; 2. Glucose; 3. Fructose; 4. Erythrose; 5. 1,6-Anhydroglucose; 6. 5-HMF.

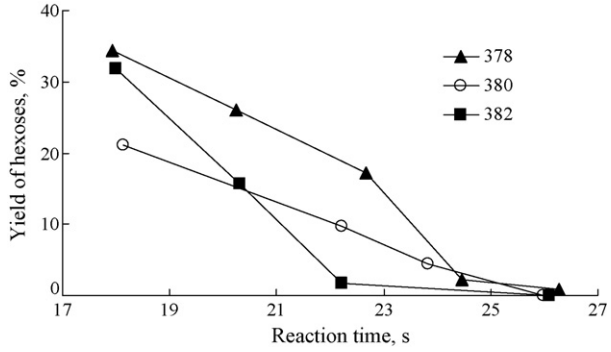

Fig. 7. Curves of yields of hexoses with reaction time longer than 18 s at 378, 380 and 382 °C.

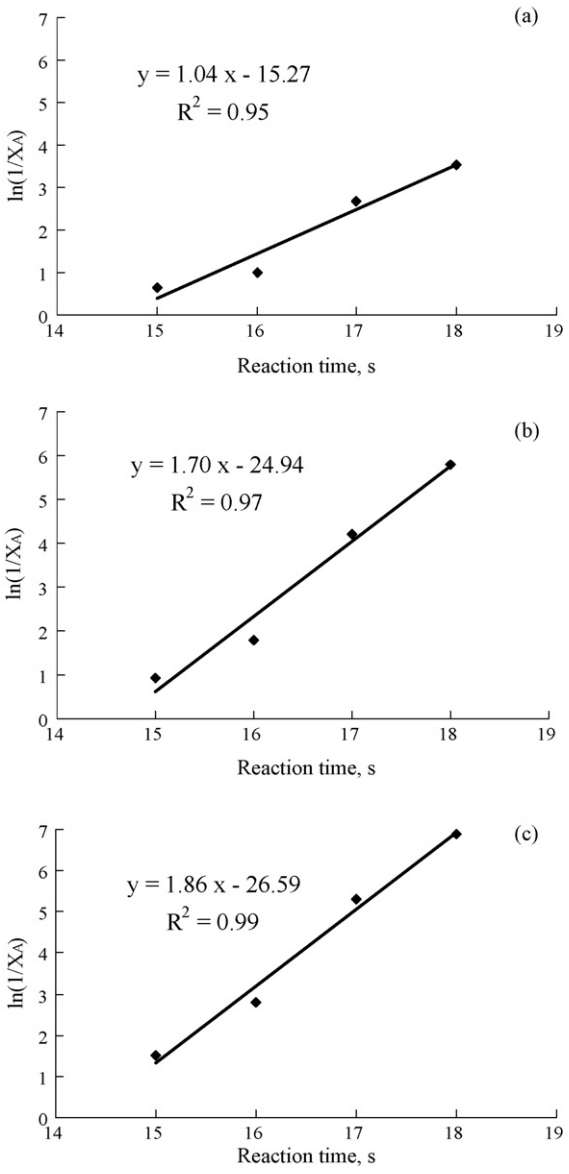

Fig. 8. Fitting lines of reaction rates of cellulose hydrolysis at (a) 378 °C, (b) 380 °C and (c) 382 °C.

4.2. Reaction kinetics of cellulose dissolution and hydrolysis

The reaction process of cellulose hydrolysis in supercritical water is subjected to the reaction kinetics of cellulose dissolution and hydrolysis, oligosaccharide hydrolysis and glucose decomposition. Sasaki et al. investigated the reaction rate constants and the other kinetic parameters of these reactions and reported that the reaction rate of cellulose hydrolysis in subcritical water is lower than that of either oligosaccharide hydrolysis or glucose decomposition [7,18]. This is primarily due to the absence of a surface contact and reaction between cellulose and water due to the crystallinity and insolubility of cellulose. However, the significant increase of solubility in supercritical water leads to a sharp increase in the reaction rate constant of cellulose hydrolysis, and the production of oligosaccharides becomes much greater than their consumption.

With respect to the reaction kinetics of cellulose and oligosaccharides, Bonn et al. performed an experiment at 240 °C and showed that the reaction rate of cellobiose hydrolysis was higher than that of glucose decomposition, while that of cellulose hydrolysis was much lower [10]. In accordance with the reaction kinetics, it is possible to obtain higher yields of hexoses by first hydrolyzing cellulose into oligosaccharides under supercritical conditions and then hydrolyzing the oligosaccharides to hexoses under subcritical conditions. Presently, an investigation for optimizing conditions for cellulose pre-treatment and hydrolysis using combined supercritical/subcritical technology is being conducted in the authors' laboratory.

5. Conclusions

The present study demonstrated that cellulose hydrolysis in supercritical water was both rapid and effective. However, it is difficult to obtain a high yield of target products, namely fermentable hexoses, using only this method. However, if we target the products to be oligosaccharides rather than hexoses, a better result can be achieved. A yield of 40% oligosaccharides and 24% hexoses was obtained under the conditions of 380 °C and 16 s. The kinetic analysis guaranteed the feasibility of direct sugar production from cellulose by separating the cellulose dissolution and first stage hydrolysis (to oligosaccharides) from the second stage hydrolysis (from oligosaccharides to hexoses). A combined supercritical/subcritical technology was proposed to achieve this purpose.

Acknowledgements

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