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Kinetic analysis for the isomerization of cellobiose to cellobiulose in subcritical aqueous ethanol

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ABSTRACT

The isomerization of cellobiose to cellobiulose, and other degradation reactions of cellobiose were investigated in subcritical aqueous ethanol with concentrations of ethanol ranging from 0 to 60% (w/w) and at temperatures ranging from 170 to 200 °C. The maximum yield of cellobiulose (ca. 40%) was obtained from the treatment of cellobiose in 60% (w/w) aqueous ethanol at 190 °C. Glucose and fructose were also detected as byproducts. The concentration-time integral method was employed to analyze the rate constants for the isomerization and degradation processes. The rate constant of cellobiose isomerization to cellobiulose was greater than those of the degradation reactions under all experimental conditions, and it increased significantly with treatment temperature and ethanol concentration. However, the use of higher temperatures and ethanol concentrations was restricted due to decomposition of the saccharides and the low solubility of cellobiose, respectively. The effect of initial feed concentration (0.5–5.5% w/w) was also studied. The maximum productivity of cellobiulose, 54.1 kg/(h m^3-reactor), was accomplished at a feed concentration of 5.5% (w/w) in 20% (w/w) subcritical aqueous ethanol.

1. Introduction

Reducing keto-disaccharides are disaccharides in which one of the constituent monosaccharides contains a free ketone group. Reducing keto-disaccharides have limited natural sources and hence are mainly synthesized by isomerization of the corresponding aldo-disaccharides [1–3]. Most reducing keto-disaccharides were initially identified as byproducts of fermentation processes [4]. At present, the use of reducing keto-disaccharides has attracted increasing attention in the food and pharmaceutical industries due to their numerous health benefits and excellent processing characteristics. For example, isomaltulose (α-D-glucose-(1 → 6)-D-fructose) can be used to suppress oral plaque formation, as a sweetener for diabetic patients, and as a diluent in tablets. In addition, lactulose (β-D-galactose-(1 → 4)-D-fructose) acts as a powerful prebiotic and can be utilized for the treatment of hepatic encephalopathy and constipation [5–10].

Cellobiulose (β-D-glucose-(1 → 4)-D-fructose) is the reducing keto-disaccharide derived from cellobiose (β-D-glucose-(1 → 4)-D-glucose), a hydrolysis product of cellulose [3]. As with other reducing keto-disaccharides, cellobiulose can be synthesized via the Lobry de Bruyn–Alberda van Ekenstein rearrangement using an alkaline catalyst [11–13]; this process is the most commonly used method for the production of industrial quantities of lactulose, a famous reducing keto-disaccharide, because of its high yield. However, the rearrangement reaction also produces a significant amount of undesirable components, necessitating tedious and expensive downstream processing to remove the catalyst and byproducts [14,15]. Because of these limitations, cellobiulose is not produced in large quantities; consequently, little is known about the physicochemical properties or potential applications of cellobiulose. Furthermore, because enzymatic production of cellobiulose has not been reported, an efficient method to produce cellobiulose is required.

In recent decades, subcritical water has been widely employed as an attractive means for the production of saccharides [16–18].

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Subcritical water is defined as liquid water between 100 and 374 °C under high pressure (usually from 1 to 6 MPa) [19]. Subcritical water can accelerate chemical reactions similar to catalyst [20–22]. Mohd Shafie et al. reported that the decomposition of cellobiose in subcritical water (200–275 °C, 10 MPa) leads to the production of 39% cellobiulose [23]. Yu et al. reported that a combination of subcritical water and alkali and alkaline earth metal chlorides, (NaCl, KCl, $MgCl_2$, and $CaCl_2$) can significantly increase the reaction rate and selectivity of cellobiose isomerization [24]. In our previous work, we have reported that the addition of ethanol to subcritical water can promote and suppress the isomerization and hydrolysis of several aldo-disaccharides, respectively [25–27].

In this study, the effects of ethanol concentration and treatment temperature on the isomerization of cellobiose to cellobiulose in subcritical aqueous ethanol were investigated. The rate constants for possible reactions during the treatment were evaluated. Moreover, the optimal cellobiose concentration for the feed was determined.

2. Results and discussion

2.1. Solubility of cellobiose in aqueous ethanol

To prevent the precipitation of cellobiose in the reactor during feeding, reaction, and cooling, the solubility of cellobiose must be known. Therefore, we carried out experiments to determine the solubility of cellobiose in aqueous ethanol. Fig. 1 shows that increasing the ethanol concentration from 0 to 80% (w/w) led to a significant decrease in solubility, from 12 to 0.3% (w/w). The solubility of cellobiose is considerably lower than that of maltose, which decreases from 36 to 1% (w/w) by changing the solvent from water to 80% (w/w) aqueous ethanol [26], and it is possible that the differences in the three-dimensional configuration of glucose affect the solubility. The low solubility of cellobiose limits the feeding of a high concentration of substrate. Therefore, we chose a feed cellobiose concentration of 0.5% (w/w) to study the effects of ethanol concentration and temperature on the isomerization of cellobiose to cellobiulose in 0–60% (w/w) subcritical aqueous ethanol.

2.2. Effect of temperature on the isomerization of cellobiose to cellobiulose

Fig. 2 shows the results of the isomerization and hydrolysis of cellobiose performed at different temperatures (170, 180, 190, and 200 °C) in 60% (w/w) subcritical aqueous ethanol. The conversion of cellobiose for a residence time of 700 s increased from ca. 44–96% (w/w) when the reaction temperature was raised from 170 to 200 °C. At 170 and 180 °C, the results of high-performance liquid chromatography (HPLC) indicate that cellobiulose was the major product of cellobiose conversion via isomerization, and glucose produced by hydrolysis was only a minor product. The maximum yield of cellobiulose at 170 °C did not exceed 21% (w/w); however, the yield increased to ca. 35% (w/w) when the temperature was raised to 180 °C. Importantly, the yield of glucose obtained from the treatment of cellobiose at 170 °C (ca. 4%) was similar to that at 180 °C. Increasing the temperature to 190 °C resulted in the maximum yield of cellobiulose (ca. 40%) at a residence time of 400 s. After 400 s, the yield decreased slightly with residence time. The yield of cellobiulose did not show a similar increase with increasing temperature, although the conversion of cellobiose at 200 °C was greater than that at 190 °C. On increasing the temperature to 200 °C, the yield of cellobiulose increased rapidly with residence time, reaching a maximum (ca. 40%) at a residence time of 200 s; however, this was followed by a decrease in yield at longer residence times. At both 190 and 200 °C, the reaction mixture contained glucose and fructose as minor products. The yields of glucose and fructose obtained from treatment at 190 °C were ca. 6 and 2% (w/w), respectively, whereas at 200 °C, the yields of glucose and fructose increased to ca. 7 and 5% (w/w), respectively. The formation of a large quantity of monosaccharides as well as the rapid and high degradation of sugars indicated that the isomerization of cellobiose to cellobiulose at 200 °C was unfavorable. Moreover, a brown-colored reaction mixture was obtained at this treatment temperature. The results of the total mass balance of sugars showed that increasing treatment temperature from 170 to 200 °C led to a decrease in the total yield of sugars from 89 to 51% at a residence time of 400 s which revealed that other degradation reactions of sugars, such as dehydration of glucose and fructose, also occur.

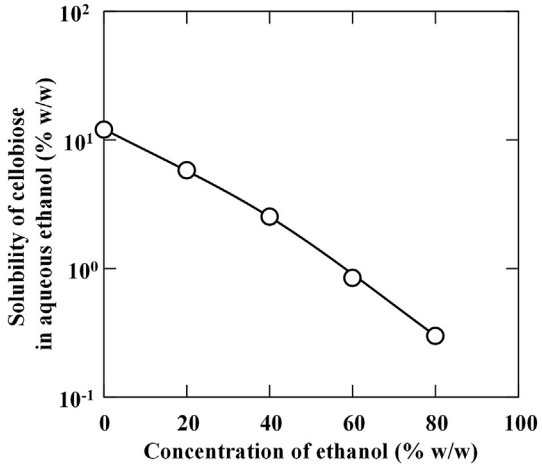

Fig. 1. The solubility of cellobiose in aqueous ethanol at 25 °C.

2.3. Effect of ethanol concentration on the isomerization of cellobiose to cellobiulose

The effect of ethanol concentration on the isomerization and hydrolysis of cellobiose at 190 °C is shown in Fig. 3. The results indicate that the conversion of cellobiose increased with increasing ethanol concentration. When cellobiose was treated for 700 s in subcritical water, the degree of conversion was ca. 51%. On increasing the ethanol concentration from 20 to 60% (w/w), the conversion of cellobiose at a residence time of 700 s rose from 62 to 86% (w/w). The yield of cellobiulose also showed a similar rising trend with increasing ethanol concentration to that observed for the conversion of cellobiose. Treating cellobiose in subcritical water produced a cellobiulose yield of ca. 17% (w/w) at a residence time of 400 s, further increasing to 40% when the cellobiose was treated in 60% (w/w) aqueous ethanol. However, monosaccharide formation did not follow the same trend as the changes in concentrations of cellobiose and cellobiulose with ethanol concentration. As a result, in subcritical aqueous ethanol (20–60% (w/w)), the yield of fructose was ca. 4% or lower, whereas in subcritical water, fructose was not found. The yield of glucose decreased from ca. 13 to 6% (w/w) when the ethanol concentration was increased from 0 to 60% (w/w) at a residence time of 700 s. These results indicated that the isomerization and hydrolysis reactions of cellobiose were promoted and suppressed, respectively, on increasing ethanol concentration.

Several studies of isomerization reactions in subcritical fluids have examined the influence of temperature and ethanol concentration. When water is heated, the hydrogen bond among water