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Effect of initial pH on hydrothermal decomposition of cellobiose under weakly acidic conditions

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HIGHLIGHTS

- Kinetics and mechanism of cellobiose hydrothermal conversion at pH 4–7 are studied.
- The rate constants of isomerization reactions remain unchanged at pH 4–7.
- The rate constant of hydrolysis reaction increases substantially with decreasing pH.
- A kinetic model is developed to simulate cellobiose decomposition at various pH.

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ABSTRACT

The paper reports the cellobiose hydrothermal decomposition at 200–250 °C under non-catalytic (with an initial pH close to 7) and weakly acidic conditions (with an initial pH of 4–6). It was found cellobiose decomposition under both non-catalytic and weakly acidic conditions follows similar primary decomposition pathways, i.e., isomerization and hydrolysis reactions being the main primary reactions. However, cellobiose decomposition under acidic conditions decreases the selectivities of isomerization reactions but increases the selectivity of hydrolysis reaction. While the rate constants of isomerization reactions under various pH conditions are found to be similar, that of hydrolysis reaction increases significantly with reducing the initial pH of the solution. Therefore, the acceleration of cellobiose decomposition under acidic conditions is mainly due to the increased contribution of hydrolysis reaction. Further analysis suggests that the rate constant of hydrolysis reaction is dependent on the hydrogen ion concentration of the solution at reaction temperature. A kinetic model was then developed, considering the isomerization and hydrolysis reactions. The model can well predict the cellobiose hydrothermal decomposition under various initial pH conditions at low temperatures (i.e., <225 °C). However, the model underestimates the rate constant of cellobiose hydrothermal decomposition at higher temperatures (i.e., 250 °C), suggesting the increased contribution of other reactions (e.g., reversion reactions) under the conditions.

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1. Introduction

Biomass hydrothermal processing is a promising technology for the sustainable production of renewable fuels and green chemicals [1–10]. Compared to ambient water, water under sub- and supercritical conditions has considerably higher ion product, which catalyses both acid and alkaline reactions [11]. Some organic acids are also produced during biomass hydrothermal conversion [12,13] and these organic acids may further promote the acid-catalysed reactions. Therefore, the chemistry of biomass hydrothermal conversion is known to be very complex [4,5].

Various reactor systems were employed for studying biomass hydrothermal reactions under different reaction conditions [4,5]. In a semi-continuous reactor system, the interactions between reactants and products are minimised and with rapid quenching it enables investigation into the primary hydrothermal decomposition of biomass or cellulose [14,15]. Biomass or cellulose is primarily converted into sugar oligomers with various degrees of polymerisation (DPs) [14,16,17], which are subsequently decomposed into sugar monomers and other smaller molecules. While the hydrothermal decomposition of sugar monomers such as glucose [18–21] is well documented, that of sugar oligomers is scarcely reported. Recently, Kimura et al [22] suggested that the hydrothermal decomposition of glucose oligomers (with DPs up to 4) at 100–140 °C proceeds by transforming the terminal glucose into fructose, followed by the breaking of glycosidic bond to

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produce fructose. As the simplest glucose oligomer, cellobiose is used as a model compound to investigate the hydrothermal conversion of glucose oligomers. At 300–420 °C, hydrolysis reaction (producing glucose) and retro-aldol reaction (producing glucosyl-erythrose, i.e., GE) are the main primary reactions during cellobiose hydrothermal decomposition [23–25]. However, at low temperatures (200–275 °C), this group recently reported [26,27] that the primary reactions are dominated by cellobiose isomerization reactions to produce cellobiulose (glucosyl-fructose, GF) and glucosyl-mannose (GM). Hydrolysis of cellobiose to produce glucose is only a minor reaction, and the retro-aldol reaction to produce GE is negligible.

It was also observed in our recent studies [26,27] that the pH value of liquid product from cellobiose decomposition reduces substantially (to a pH value of ~4) even at early stage of cellobiose decomposition (i.e., with conversion of ~20%) under non-catalytic conditions [27]. This indicates that the reaction condition during cellobiose decomposition changes from hydrothermal to weakly acidic (pH = 4–6) as cellobiose decomposition proceeds. Several previous studies were undertaken on the hydrolysis of cellulose [28–30], glucose [31–33] and cellobiose [12] in dilute acid. However, those previous studies were mostly conducted under acidic conditions with pH < 3 where acid-catalysed reaction plays a dominant role. Under weakly acidic conditions (pH = 4–6), the cellobiose decomposition was reported to follow a distinctly different reaction mechanism to those under stronger acidic conditions (i.e., pH < 3) [12]. Unfortunately, the fundamental reaction mechanism of cellobiose decomposition under such weakly acidic conditions (pH = 4–6) is still largely unclear.

Therefore, the purpose of this study is to compare cellobiose decomposition at 200–250 °C under non-catalytic (pH close to 7) and weakly acidic (pH = 4–6) conditions. This study will provide a mechanistic understanding into the fundamental reactions of cellobiose hydrothermal decomposition to build a linkage between non-catalytic and acidic conditions.

2. Experimental section

2.1. Materials and reactor system

Cellobiose, chemical standards and reagents used for this study were purchased from Sigma–Aldrich, except GF and GM that were purchased from LC Scientific Inc. (Canada). Sulphuric acid was used to prepare the cellobiose solution at different pH values. A continuous stainless tube reactor system was used for cellobiose decomposition experiments at 200–250 °C, with the reactor system description detailed elsewhere [21,26]. Briefly, a cellobiose solution (at a particular pH) was fed by an HPLC pump, and then heated by a stream of preheated water delivered by another HPLC pump before entering the reactor. The ratio of flow rates between the preheated water and the cellobiose solution was 2:1. After mixing, the final concentration of the reactant is controlled to be ~1 g L^{-1} with the pH values of 4–7. The reaction temperature at the mixing point is monitored by a thermocouple to ensure that the temperature of solution is rapidly increased to reaction temperature before entering the reactor. Upon the completion of the experiment, the liquid product from the reactor was rapidly quenched by an ice bath, and then the sample was collected for analysis. The pressure of the reactor system was maintained at 10 MPa using a back-pressure regulator.

2.2. Sample analysis

The liquid samples before and after reaction were analysed using a Dionex ICS-5000 ion chromatography system with pulsed amperometric detection and mass spectrometry (HPAEC-PAD–MS). A gradient method [26] was used for identifying and quantifying the compounds in the liquid samples. The experiments were repeated at least three times and the standard error was shown in the figures. Based on the concentrations of various compounds in the liquid sample, the cellobiose conversion, the yield and the selectivity of a compound can be calculated on a carbon basis, according to the method used in our previous paper [27]. The pH value of liquid samples before and after reaction was measured by an acid-base titrator (MEP Oil Titrino plus 848). The carbon content of the liquid sample was measured by a total organic carbon (TOC) analyser (Shimadzu TOC-V_{CPH}). The gas production during cellobiose decomposition in this study was negligible.

2.3. Calculation of hydrogen ion concentration at a given reaction temperature

The hydrogen ion concentration at a given reaction temperature can be estimated based on the dissociation of both sulphuric acid and water at reaction temperature [29,31]. The H^+ and OH^- ion concentrations in high temperature water are higher than those in ambient water and the H^+ ion concentration in water at a temperature (T) can be calculated using Eq. (1):

$$[H^+]_{W,T} = \sqrt{K_{W,T}} \tag{1}$$

where $K_{W,T}$ is the ionisation constant of water at T (K) and its value at 200–250 °C can be found elsewhere [34].

The dissociation of sulphuric acid to release hydrogen ions takes place in two steps:

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^- \quad \text{(1st Dissociation)}$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \quad \text{(2nd Dissociation)}$$

According to Oscarson et al. [35], the dissociation constants of the first reaction is between 5.8 and 2.6 M at 200–250 °C, with a complete dissociation generally accepted for the first dissociation reaction. The second dissociation constant can be calculated based on following equation [36]:

$$LogK_{2,T} = 56.889 - 19.8858LogT - 2307.9/T - 0.006473T \tag{2}$$

This equation is applicable for temperatures between 25 and 350 °C. Then, the hydrogen ion concentration for sulphuric acid at T can be determined based on following equation:

$$[H^+]_{SA,T} = C_{SA,0} + 0.5\left(-C_{SA,0} - K_{2,T} + \sqrt{(C_{SA,0} + K_{2,T})^2 + 4C_{SA,0}K_{2,T}}\right) \tag{3}$$

where $C_{SA,0}$ is the initial sulphuric acid concentration (mol L^{-1}). Consequently, the total hydrogen ion concentration (mol L^{-1}) at a given reaction temperature can be calculated as:

$$[H^+]_T = [H^+]_{W,T} + [H^+]_{SA,T} \tag{4}$$

3. Results and discussion

3.1. Effect of initial pH on the yields of primary products from cellobiose decomposition

Fig. 1 presents the data on the effect of initial pH on the yields of cellobiose and its main primary products as a function of residence time at 200–250 °C. It is clearly shown that the cellobiose yield decreases with decreasing initial pH of cellobiose solution from close to 7 (i.e., water only) to 4 at all temperatures. Obviously, the addition of acid promotes the cellobiose hydrothermal conversion. It is also interesting to see that the isomerization reaction products GF and GM are also produced as major primary products

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