Conversion Mechanism of Cellulosic Biomass to Lactic Acid in Subcritical Water and Acid–base Catalytic Effect of Subcritical Water

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The conversion mechanism of cellulosic biomass to lactic acid in subcritical water without the addition of any alkaline catalyst is discussed. Results showed that this conversion mechanism appears to follow the same pathways elucidated in the conversion of sugar to lactic acid in an alkaline solution. Further, it is suggested that water in the subcritical region may act as an effective acid–base catalyst.

Our study involving the conversion of cellulosic biomass into useful products by hydrothermal treatment showed that a considerably high amount of lactic acid was also formed, as well as HMF and 2-FA, at 250–350 °C. It is generally known that lactic acid is a product of alkaline degradation of sugar, and the conversion mechanism of sugar to lactic acid in alkaline solution is well established by Nef[1,2] and Evans[3] with some modifycations afterward. This is known as the traditional theory. However, the conversion mechanism of cellulosic biomass to lactic acid in subcritical water is not yet fully understood. In this study, the conversion mechanism of cellulosic biomass to lactic acid in subcritical water without the addition of any catalyst was investigated, and the acid–base catalytic effect of subcritical water was also discussed.

Cellulose and glucose were used as the main test materials. The cellulose used was a filter paper powder (more than 200-mesh in size), and the glucose was of reagent grade. Other chemicals, such as fructose, glyceraldehyde, dihydroxyacetone and pyruvaldehyde were also used as test materials. All experiments were carried out with a batch reactor made of SUS 316 with an internal volume of 5.7 cm^3, described earlier.[4] Briefly, a 0.07 g (dry base) test material and 3.4 cm^3 of water (60% water fill) were added into the reactor, and then the sealed reactor was put into a salt bath that had been preheated to 300 °C. After a certain reaction time, the reactor was removed from the salt bath, and then put into a cold-water bath to quench the reaction. All experiments were carried out at a constant salt bath temperature of 300 °C and for 30 s (120 s for cellulose). A residential time that reactor is kept in the salt bath is defined as a reaction time. Real reaction time at 300 °C is shorter than 30 s, because heating of the reactor to 300 °C required about 15 s. The pressure in reactor was ca. 8.9 MPa. After the reaction, a solution sample was collected and analyzed.

To investigate the conversion mechanism of cellulosic biomass to lactic acid under the hydrothermal reaction, the intermediate products for hydrothermal degradation of cellulose and glucose were identified in detail by HPLC, with auxiliary analyses by NMR and GC/MS analyses if necessary. Figure 1 shows the results of HPLC analyses. Fructose and some C_3 carbon compounds such as glyceraldehyde, dihydroxyacetone, and pyruvaldehyde were identified, as well as lactic acid and residual glucose. Fructose may come from the isomerization of glucose by the Lobry de Bruyn–Alberda van Ekenstein (LBAE) transformation, which has been well-studied by a number of researchers in carbohydrate chemistry, and has been commonly known to occur in alkaline media because an alkaline condition usually promotes isomerization. Some recent studies[5,6] also reported that fructose was formed in the hydrothermal treatment of glucose with or without addition of an alkaline catalyst.

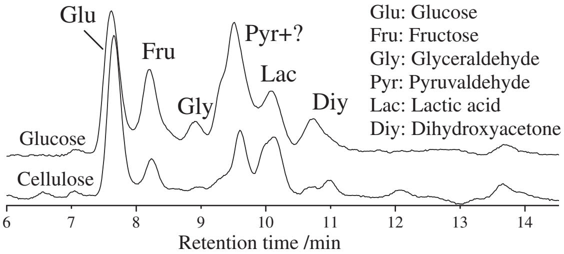

Figure 1. HPLC chromatograms for cellulose and glucose after reaction at 300 °C and 30 s for glucose, 120 s for cellulose (Column: SUGAR SH1011, Detector: RI, Fluent: 2 mM $HClO_4$, Flow rate: 1.0 mL/min, Temp: ambient).

The C_3 carbon compounds are likely the products involved in the formation reactions of lactic acid, because they are also formed in the conversion of sugar in alkaline solution to lactic acid and are considered to be sources of lactic acid in alkaline solution according to the traditional theory. That is, both glyceraldehyde formed by the reverse aldol condensation of fructose and dihydroxyacetone which is considered to be the isomerization of glyceraldehyde loses water to form pyruvaldehyde, and pyruvaldehyde subsequently undergoes a benzilic acid rearrangement to form lactic acid. Antal et al.[7,8] discussed the formation mechanism of lactic acid from the C_3 compounds by employing the traditional theory in alkaline solution.

On the basis of identified intermediates and the traditional theory of conversion of sugar to lactic acid in alkaline solution, and combining our experimental findings in the hydrothermal treatment of glucose and/or fructose, a mechanism for the formation of lactic acid from glucose in subcritical water was systematically interpreted as shown in Figure 2. At first, because fructose was identified, it was assumed that glucose first undergoes isomerization to fructose by the LBAE transformation. Conversely, fructose may convert to glyceraldehyde. An experiment with fructose showed the formation of a considerably high amount of glyceraldehyde (see Figure 3).

At the same time, glyceraldehydes may rearrange into dihydroxyacetone by the LBAE transformation. To test if this mechanism existed in our experimental reactions, an experiment with glyceraldehydes was performed. As shown in Figure 4, a strong peak at 19.5 min was observed. It indicates that the isomerization of glyceraldehyde and dihydroxyacetone occurred in our experimental condition.

A possible co-product with fructose, if LBAE transformation occurs, would be glucose 1,2-enediol, because LBAE transformation of glucose would give a series of enediol as well as fructose. Glyceraldehyde would be formed by cleavage of glucose 1,2-enediol, because the formation of a double bond between carbon 1 and carbon 2 in glucose 1,2-enediol weakens the single bond between carbon 3 and carbon 4 in accordance with the double bond rule. Recently Kabyemela et al.[5] also suggested that this mechanism existed in sub/supercritical water. However, in the present study, glucose 1,2-enediol was not detected. This could probably be due to its instability.

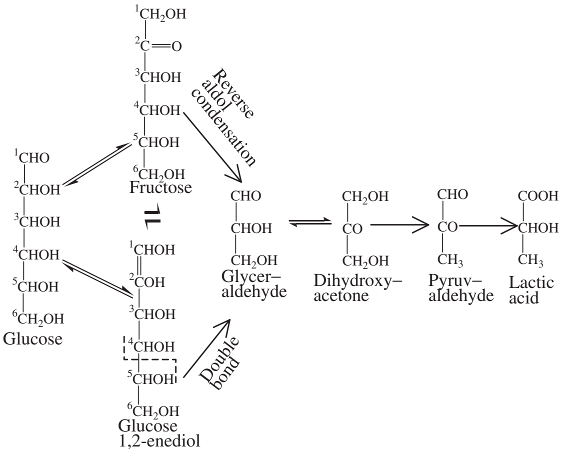

Figure 2. Proposed pathways of conversion of glucose to lactic acid in subcritical water.

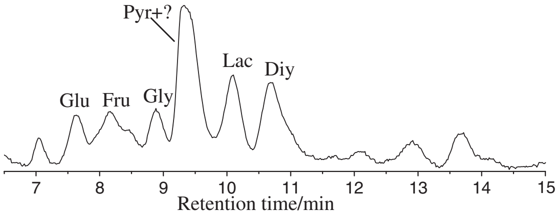

Figure 3. HPLC chromatogram of degradation of fructose at 300 °C, 30 s (Analytical condition is same as Figure 1).

Further, both glyceraldehyde and dihydroxyacetone may lose water to form pyruvaldehyde, which subsequently undergoes a benzilic acid rearrangement to lactic acid. According to this mechanism, pyruvaldehyde would be formed in the hydrothermal treatment of glyceraldehyde and dihydroxyacetone, and lactic acid would be the major product in the hydrothermal treatment of pyruvaldehyde. As expected (see Figure 4), pyruvaldehyde was formed in experiments involving both glyceroldehydes and dihydroxyacetone as reactants, and lactic acid was the major product in the experiment involving pyruvaldehyde as a reactant. It should be noted that according to the traditional theory, the benzilic acid rearrangement of pyruvaldehyde to lactic acid commonly occurs in alkaline solution, because pyruvaldehyde is an α-diketone, and when treated with a base, α-diketones rearrange to give the corresponding saccharinic acids. The formation of large quantities of lactic acid in the experiment with pyruvaldehyde may indicate that the benzilic acid rearrangement occurs in subcritical water even in the absence of the addition of an alkaline catalyst. The mechanism so far discussed may imply that the conversion of glucose to lactic acid in subcritical water appears to follow the same pathways elucidated in the conversion of sugar to lactic acid in alkaline solution. This means that subcritical water may act as an effective Brønsted base catalyst.

Additionally, as reported in our previous study,[9] a large quantity of HMF and 2-FA, known as products of the facile, acid-catalyzed dehydration of hexoses and pentoses, were formed. The possibility of the formation of HMF and 2-FA is supposed to be due to autocatalysis (as by acidic initial products). An experiment with formic and acetic acids, to recognize the potential for autocatalysis by formic and acetic acids, showed that acetic and formic acids did not reveal a significant catalytic effect. These results indicate that subcritical water may act not only as Brønsted base catalysts but also as acid catalysts. The most likely source of hydroxide and hydroxide ions is the high temperature water itself because subcritical water has a stronger tendency to ionize than ambient water, which makes water a Brønsted base-acid and act as an effective catalyst. Moreover, the highest yields of HMF, 2-FA and lactic acid were obtained in the same temperature range of 280–300 °C, which may be related to the fact that the ionization constant at the saturation pressures reaches a maximum in this temperature range.

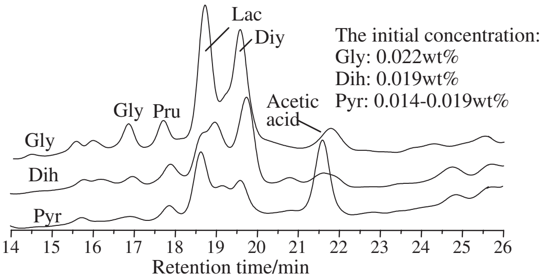

Figure 4. HPLC chromatograms of hydrothermal degradation of glyceraldehyde, dihydroxyacetone and pyruvaldehyde at 300 °C, 30 s (Column: Shodex lonpak KC–811 × 2, Detector: UV–210 nm, Fluent: 2 mM $HClO_4$, Flow rate: 1.0 mL/min, Temp.: 50 °C).

To further confirm the action of acid–base catalysts of high temperature water on glucose decomposition, glucose was treated with the addition of either H_2SO_4 or NaOH. The result was that lactic acid in the experiment with H_2SO_4, and HMF and 2-FA in the experiment with NaOH were still identified, when the concentration of H_2SO_4 or NaOH was 0.02 mol/L. This indicates that base-catalyzed reactions occurred even with the addition of an acid catalyst, and acid-catalyzed reactions occurred even with the addition of a base catalyst. This means that subcritical water may act as a strong acid–base catalyst.

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