The investigation of degradation reaction of various saccharides in high temperature and high pressure water

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Abstract. Recently, conversions of polysaccharides included in biomass resources have been studied in order to recover valuable chemicals. Degradation of polysaccharides has been attracted by many researchers, whereas by-products from secondary reactions of the materials have not been studied very well. For the purpose of understanding reaction behavior of various monosaccharides in high-temperature and high-pressure water regions, we investigated reaction pathway and kinetics through reaction experiments of degradation of saccharides in subcritical water. The experiment was conducted by using continuous flow-type micro-reactors. Glucose was used as the starting material. From the experimental results, the conversion of glucose increased with increasing the residence time. The yields of fructose and 1,6-anhydro-\(\beta\)-D-glucose decreased with increasing the residence time. The yields of organic acids and some aldehydes increased with increasing the residence time.

1. Introduction

In recent years, the energy consumption is increasing in all over the world. The growth in consumption of energy in 2001 is three times as high as its 1965 [1,2]. Fossil fuel is used for the automobiles and the industrials, and it causes the elevation in carbon dioxide concentration in the atmosphere. From these facts the biomass is receiving attention for its capability as an alternative to fossil fuels as a chemical resources. Cellulose hemi-cellulose and lignin are main components of biomass. Especially cellulose is contained as a constituent element of biomass. It is also able to convert into energy in diverse ways. In conventional techniques, for example, a dilute sulfuric acid method [3] is representative as one of reaction methods. The dilute sulfuric acid method, 0.1 ~2.0 % of acid concentration, 130~240 °C of reaction temperature, leads to recover useful chemicals as decomposition products. Although these decomposition methods use sulfuric acid or hydrochloric acid as catalysts, it makes treatment process cumbersome and complicated by the treatment of the harmful catalyst which remains after the process. Therefore, in the conversion of the biomass to the utilization science material, the low-loaded material is selected for environment and development of the new synthetic method of the environment fitter type and high economic efficiency is desired. Consequently we focus on water as the solvent that is low load to the human body, and advance the research of the conversion method of the biomass under the non-catalytic condition. Because sub-critical and supercritical water have many interesting properties [4], it is widely used as the solvent of extraction and crystallization. In the previous works, a lot of study results that decompose saccharide with sub-critical and supercritical water are reported [5-9]. In this study, we carried out the experiments of...
conversion of D(+)‐glucose under sub‐critical water condition to investigate thermal stability of saccharide.

2. Experimental

2.1. Materials
D(+)‐glucose which used in the experiment starting material is purchased from Wako Pure Chemicals Industries Ltd. Regents used for products analysis were D(‐)‐fructose, DL‐lactic acid, formic acid, acetic acid also provided by Wako Pure Chemicals Industries Ltd. 5‐hydroxymethyl‐2‐furfural and glycolic acid were from Sigma‐Aldrich Co. The other regents such as 1, 6‐anhydro‐β‐D‐glucose and 2‐furufural were obtained from Tokyo Chemical Industry Co., Ltd. and Kishida Chemicals Co., Ltd., respectively.

2.2. Experimental
Fig. 1(a), (b) show the schematic diagram of the continuous flow reactor.

For the reactor A1, the reactor was made of 1/8 inch stainless steel tubing (SUS316). The liquid solution is sufficiently degassed by the ultrasonic and the aspirator. After that the solution is disposed with high pressure pump. First the preheating water was fed to the system by the HPLC pump (NIHON SEIMITSU KAGAKU CO., LTD, model NPL‐3300). The pressure in the reactor was adjusted by the back pressure regulator (AKICO Co., Ltd, model HPB‐450). After the pressure in the system became the prescribed value and stable, heating the electric furnace was initiated. The reactor and the furnace temperature were measured by a K‐type thermocouple. After the temperature of the reactor reached at preset temperature and stable, the pump was switched to the starting material pump (JASCO Co., model BIP‐1). The concentration of glucose in the solvents was prepared at 1.5‐10 wt%. The reaction pressures were adjusted in the range from 15 to 20 MPa. The reaction temperatures were adjusted in the range from 200 to 280 °C. At the reactor, the feed solution was promptly heated to its reaction temperature and the reaction was initiated. The residence time of the solution in the reactor, τ, was evaluated by the following equation:

\[ \tau = \frac{V}{Q} \]

Figure 1(a). The schematic diagram of the continuous flow reactor (reactor A1).

Figure 1(b). The schematic diagram of the continuous flow reactor (reactor A2).
\[ \tau = \frac{V}{F} \times \frac{\rho_{T,P}}{\rho_{T,0,P}} \]  

(1)

where \( V \) is the reactor volume, \( F \) is the flow volume, \( \rho_{T,P} \) and \( \rho_{T,0,P} \) indicate the density of water at the reaction temperature and at the normal condition of water, respectively. After the reactant had passed through the reactor, the residence time was from 40 to 120 seconds which was evaluated eq 1, the flow was quenched by double tube type heat exchanger to terminate any further reactions. After that the flow was subsequently decompressed by passing through the back-pressure regulator.

For the reactor A2, the application was conducted with two pumps. The condition of experiment was same to reactor A1 except for mixing preheated water and starting material.

The identification and quantitative analysis of the each product were conducted by HPLC-UV/RI. 0.003 mol/L perchloric acid was used as the mobile phase, and BTB solution was used as coloring reagent to detect organic acids, and it mixed in the immediate aftermath of the column. For evaluating the carbon balance, a total organic carbon analyzer (Shimadzu, Model TOC-5050A) was used. The conversion (\( X \)) and the yield (\( Y \)) were evaluated by following equations (2, 3) [10]:

\[ X = \left(1 - \frac{C_f}{C_0}\right) \times 100 \]  

(2)

\[ Y = \frac{C}{C_0} \times 100 \]  

(3)

where \( C_0 \) is the initial concentration of the starting material, \( C_f \) is the concentration of ingredient in product, and \( C \) is product concentration.

3. Result and discussion

Figure 2 shows the HPLC-RI/UV chromatogram of the products from glucose as treated in sub-critical water. From HPLC-RI chromatogram, the main products are D-fructose, 1,6-anhydro-\( \beta \)-D-glucose, glycolaldehyde, 5-HMF, and 2-furfural. From HPLC-UV chromatogram, glycolic acid, lactic acid, acetic acid, and formic acid are observed.

![HPLC chromatogram of the products: \( T = 240^\circ \text{C}, P = 20 \text{ MPa}, \tau = 60 \text{ sec, 6 wt\%}, \text{reactor A1. (a) RI chromatogram, (b) UV chromatogram.} \](a) (b)

These chemicals also can confirm in main reaction pathway which suggested in previous works. D-glucose isomerizes into fructose or dehydrates into 1,6-anhydro-\( \beta \)-D-glucose, glycolaldehyde, 5-HMF, and 2-furfural. On the other hand, the organic acids are obtained from secondary reaction of these products. It is thought that 5-hydroxymethyl-2-furfural (5-HMF) is a dehydration product of D-fructose which is an isomer of the D-glucose.
Figure 3(a), (b) show results at 240 °C, 20 MPa, 3 wt%. From figure 3(a), in this case, the conversion of D-glucose increased in increasing the residence time. At 120sec, the conversion became 83.1 %. The yield of 2-furufural that is one of the dehydration product of D-glucose was obtained in high yield at longer residence time. This result indicates that the dehydration reaction was occurred with D-glucose. D-fructose which is an isomer of D-glucose was observed more high concentration in the short residence time. This reaction is supposed to be caused by keto-enol tautomerization. 5-HMF was formed in high yield at the longer residence time. This result expresses that the dehydration reaction occurred with D-fructose. For the yield of organic acids, almost all products were obtained in high yield at the longer residence time. Especially, the yield of formic acid reached at about 11.9 %.

![Graphs showing the products yield and conversion of glucose](image)

Figure 3. The products yield and the conversion of glucose: $T = 240$ °C, $P = 20$ MPa, 3 wt%. (a), (b): The products yield and the conversion using the reactor A1. (c), (d): The products yield and the conversion using the reactor A2.

symbols: + Conversion, ● fructose, ▲ glycolaldehyde, × 1,6-anhydro-β-D-glucose, ◯ 5-HMF, ● 2-furfural, ○ glycolic acid, △ lactic acid, ◊ formic acid, □ acetic acid

For the reactor A2, though the conversion value was smaller than that of the reactor A1, a similar tendency was observed in the products. Moreover the comparison of the yields at almost same conversion between the reactor A1 and reactor A2 were conducted. At 240 °C, 20 MPa, 3 wt%, 53.7 % (t=40sec, reactor A1) and 54.8 % (t=122 sec, reactor A2) of the conversions of the D-glucose, it was observed that the product yields of the reactor A1 was higher than that of the reactor A2.

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References

[1] The Energy Data and Modeling Center The Institute of Energy Economics 2003 EDMC Handbook of Energy & Economic Statics in Japan (Japan: The Energy Conservation Center) pp 29-40, 175-178, 191-194

[2] The Energy Data and Modeling Center The Institute of Energy Economics 2004 EDMC Handbook of Energy & Economic Statics in Japan (Japan: The Energy Conservation Center) p 217

[3] Z. Yu and H. Zhang 2003 Bioresource Technology 40 95-100

[4] Sako T 2001 Supercritical fluid (Tokyo: Agune Syoohu sha) pp 49-68

[5] Ehara K and Saka S 2005 J. Wood. Sci., 51, 148-153

[6] Sakaki T, Shibata M, Sumi T, Yasuda S, 2002 Ind. Eng. Chem. Res., 41, 661-665

[7] Kabyemela B.M, Adsciri T, Malaluan R.M, Arai K 1999 Ind. Eng. Chem. Res., 38, 2888-2895

[8] Sasaki M and Arai K, 2002 ECO INDUSTRY, 7(1), 42-51

[9] Goto K, Tashima M, Sasaki M, Adsciri T and Arai K 2001 Kobunshironbunshu, 58(12), 685-691

[10] Sasaki M, Furukawa M, Minami K, Adsciri T and Arai K 2002 Ind. Eng. Chem. Res., 41, 6642-6649