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Solvothermal treatment of starch for the production of glucose and maltooligosaccharides

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Starch was hydrothermally degraded without any additives over the temperature range from 453 to 563 K at a constant pressure of 10 MPa and the fluid residence times up to 6 min in a semi-batch reactor to produce glucose and maltooligosaccharides. The effects of reaction temperature, flow rate of hot water and residence time of water-soluble components on the product distribution in the solvothermal degradation of starch were investigated. Even at the lowest reaction temperature studied, the loaded starch was partially degraded and dissolved within 8 min by contacting high-temperature and high-pressure water in a semi-batch reactor. By installing a plug-flow reactor at the exit of the first reactor to increase and control precisely the residence time, the maximum glucose yield of 43.8% on the carbon weight basis of the starting material was obtained at 3.64 min and 513 K. The comparison of yields of glucose and 5-hydroxymethyl furfural (HMF), which is a major secondary product, indicates that adjusting the residence time was the most effective to increase the glucose yield and to suppress the 5-HMF production.

1. Introduction

Biomass is a renewable organic resource that could be considered as a chemical feedstock having low environmental impact. The representatives of biomass are carbohydrates. Although the most abundant carbohydrates are cellulose and hemicellulose, starch is also an important polysaccharide because they are very familiar with our daily life [1]. Starch is a carbohydrate consisting of glucose units containing amylose and amylopectin, which contribute to varying starch properties [2].

Starch is contained in large quantity in wastes discharged from food and textile industries and in agriculture, and the wastes cause serious disposal problems. Many researchers studied the conversion of starch-containing wastes to fuels, chemicals and animal feeds by the use of microorganisms or enzymes [3–6]. These biological processes are promising because they need only small amount of acid/base for pH adjustment, and the biological treatments are often carried out around ambient temperature. However, relatively long treatment time is required in biological processes.

Recently, starch or starch-containing biomass was hydrolyzed to oligo- and monosaccharides in high-temperature and high-pressure water without any additives [7, 8]. It is reported that in water at elevated temperatures and pressures, polysaccharides can be hydrolyzed in the absence of acids [9–15] because of the higher ion product of water than that at ambient condition [16]. The degradation reaction in high-temperature water or any solvent is called hydrothermal degradation or solvothermal degradation, respectively. The hydrothermal processes have an advantage of short reaction time, and are free of chemicals. These benefits indicate that the hydrothermal degradation is an environmentally benign method for producing mono- and oligosaccharides from polysaccharides. In our previous work [7], starch was hydrothermally degraded in a small batch reactor, and glucose and maltooligosaccharides were mainly obtained. Glucose is utilized as a substrate for the fermentation to produce useful chemicals and fuels, and maltooligosaccharides are used in a variety of applications, which include the food and pharmaceutical industries [17].

In this study, starch was hydrothermally degraded in a semi-batch reactor combined with a plug-flow reactor (PFR) to produce glucose and maltooligosaccharides. The effects of reaction temperature, flow rate of hot water and

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residence time of water-soluble (WS) components eluted from the semi-batch reactor on the product distribution were investigated.

2. Experimental

Starch derived from sweet potato (Wako Chem. Ind., Osaka, Japan) was degraded under hydrothermal conditions in a tubular semi-batch reactor sometimes additionally installing a PFR, made of stainless-steel tubing (SUS 316, 2.17 mm I.D., 3, 6 and 9 m long), at the exit of the first reactor. The schematic diagram of the experimental apparatus with the PFR is illustrated in Fig. 1. The experimental apparatus and procedures without a PFR are essentially the same as those of the previous report [14], and briefly described below. The initial sample, i.e., 0.3 g of starch that had been dried overnight at 373 K in an air oven, was loaded in a reactor. A frit disk with pore size of 2 μm was placed at the exit of the first reactor to fix the water-insoluble substances. Distilled water was supplied by a HPLC pump (model L-6000; Hitachi, Tokyo, Japan) to the reactor through a preheating column. Starch was partially degraded and dissolved by contacting high-temperature water, and then the WS components were eluted out of the reactor through a frit disk. When the PFR was not placed, the effluent was immediately mixed with distilled water at ambient temperature pumped by another HPLC pump (model PU-2080; Jasco, Tokyo, Japan) to quench the solution rapidly. The solution was collected at certain intervals through a back-pressure regulator (model 880-81; Jasco, Tokyo, Japan) which adjusted the system pressure at 10 $\pm$ 0.1 MPa. Reactor temperature was maintained with a molten salt bath, whose temperature was regulated within temperature fluctuation of $\pm$2 K, over the temperature range from 453 to 563 K. The flow rate of distilled water supplied to the reactor was set at 5, 3, 1 or 0.5 g/min and the flow rate of distilled water for the quenching was fixed at 5 g/min. The heating time was counted from the moment when the preheater and the reactor were immersed in the molten salt bath. The reactor temperature was measured with a thermocouple inserted in the reactor. Note that the residence time of the fluid between the exit of the reactor and the sampling point was determined to be about 30 s from the tracer response measurement.

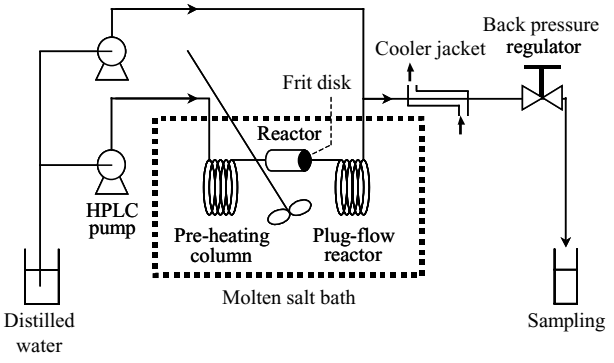

Figure 1 Schematic diagram of the experimental apparatus.

TABLE I Residence times of water in PFR at various temperatures and lengths of PFR

Length of PFR (m)	0	3	6	9
Reaction temperature (K)	Residence time (min)			
453	0	1.98	3.96	5.94
473	0	1.93	3.87	5.80
493	0	1.88	3.76	5.64
513	0	1.82	3.64	5.46

The effect of residence time of WS components on the product distribution in the hydrothermal degradation of starch was studied by installing a PFR at the exit of the first reactor. The degradation of the WS components eluted from the first reactor was carried out in the PFR over the temperature range from 453 to 513 K by immersing the preheating column, the first reactor and the PFR in the molten salt bath. Note that the flow rate of distilled water was kept constant at 5 g/min in the experiments with the PFR. The residence time was varied by replacing the PFR having different inner volumes. In this work, the residence time was referred to as that in the PFR. By assuming that the solution moved in the plug flow, the residence time t [min] of the fluid in the PFR was calculated by:

$$t = \frac{\rho V}{Q}$$

where ρ is the density of the fluid [g/cm^3], V is the inner volume of the PFR [cm^3], and Q is the mass flow rate of the hot water [g/min]. It was also assumed that the fluid density was equal to that of pure water under the same condition. Since the system pressure was fixed at 10 MPa, the density of the fluid varied with temperature. The residence times studied at different reaction temperatures with the different lengths of the PFR are tabulated in Table I. The residence time in a 9 m long PFR at 513 K was approximately shorter by 0.5 min than that at 453 K because of the lower density of water. However, the variations of the residence times with the same PFR length at each temperature are smaller than 10% of the whole residence times.

The recovered solution was analyzed for the contents of total organic carbon (TOC) by a total carbon analyzer (model 5000A; Shimadzu, Kyoto, Japan). Molecular weight distribution (MWD) of the hydrothermal degradation products of starch was determined by a HPLC using a gel-permeation chromatography (GPC) column (SB-803

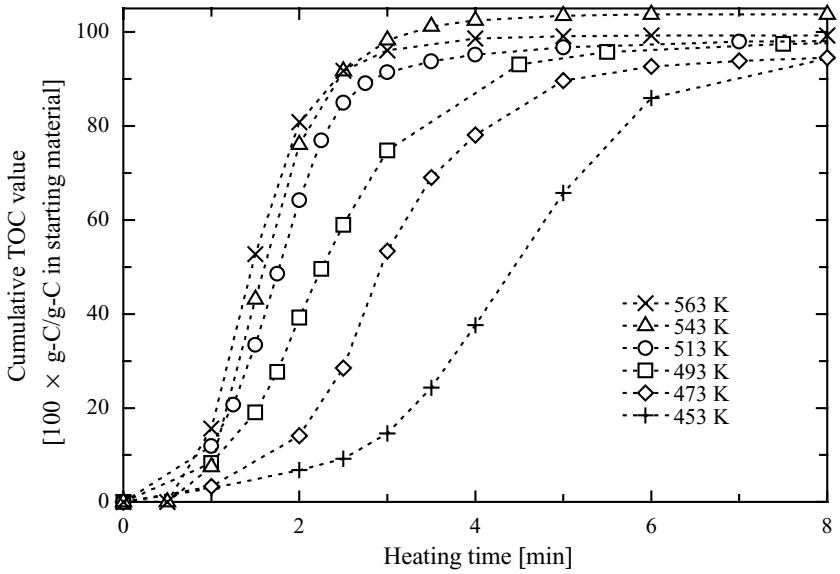

Figure 2 Time progress of cumulative TOC value at various reaction temperatures at a flow rate of 5 g/min.

HQ; Shodex, Tokyo, Japan). Produced saccharides and secondary decomposition products were quantified by a HPLC equipped with a UV and a refractive index detector by using a SH1821 column (Shodex, Tokyo, Japan). The products were identified by comparing the retention times of the peaks of reaction products with those of standard samples. In some cases, maltooligosaccharides in the recovered solution were completely hydrolyzed to glucose in 0.5 M sulfuric acid solution at 373 K for 3 h, followed by the HPLC measurements of total WS saccharides. Maltooligosaccharides with degree of polymerization (DP) up to 7 and 1,6-anhydroglucose (also referred to as levoglucosan) were quantified by a high performance anion exchange chromatograph using a CarboPac PA1 column (Dionex, Sunnyvale, CA, USA). The production of oligosaccharides was confirmed by a matrix-assisted laser desorption/ionization mass spectrometry by using AXIMA-CFR (Shimadzu, Kyoto, Japan).

3. Results and discussion

3.1. Effect of reaction temperature

Starch, which is essentially a water-insoluble polysaccharide, was partially degraded and dissolved by contacting high-temperature liquid water in the reactor, and the WS components were eluted and collected. The effect of temperature on the time progress of cumulative starch conversion based on TOC is shown in Fig. 2. Note that the flow rate of distilled water was fixed at 5 g/min, without a PFR installed. At the lowest temperature studied (453 K), it took about 8 min to degrade partially and dissolve the most of the loaded starch. The elution rate obviously became faster as the reaction temperature increased. However, the elution histories at temperatures higher than

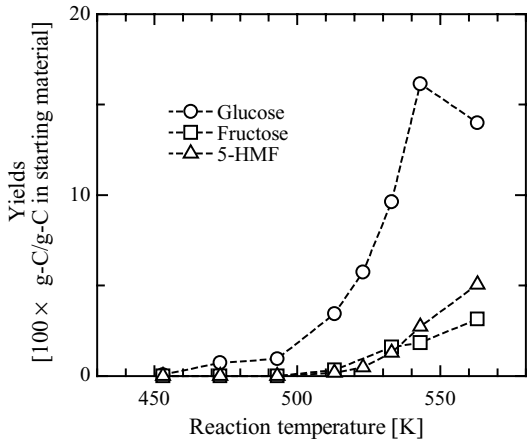

Figure 3 Cumulative yields of glucose, fructose and 5-HMF vs. reaction temperature at a flow rate of 5 g/min.

513 K were not significantly altered. At 563 K, which is the highest temperature in this work, over 90% of the original starch sample turned into WS components within 2.5 min. The reactor temperature quickly rose to prescribed values. Because the reactor temperature reached 90% of the intended values within 40 s, the elution of starch degraded partially and dissolved during the heat-up period is not significant. Note that since TOC recovered in the product solution was higher than 95% at all temperatures studied, the gaseous products and solid residues seemed to be scarcely formed. In fact, solid residue was not observed in the reactor when the reaction was completed.

The cumulative yields of glucose, fructose and 5-hydroxymethyl furfural (HMF) are plotted against reaction temperature in Fig. 3 when a PFR was not

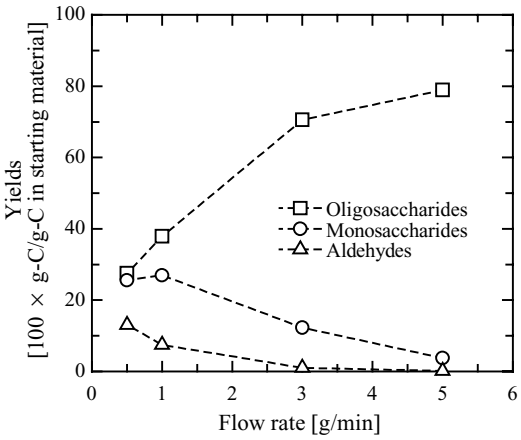

Figure 4 Cumulative yields of oligosaccharides, monosaccharides and aldehydes vs. flow rate at 513 K.

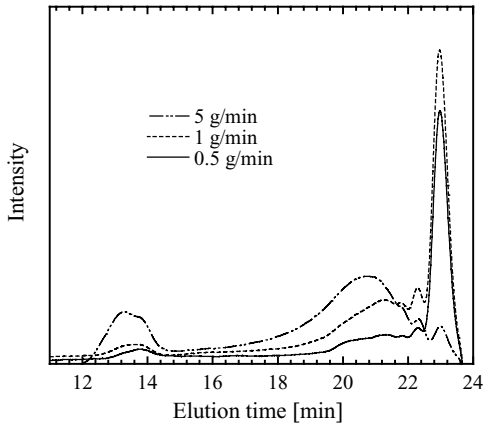

Figure 5 GPC chromatograms obtained at 513 K and different flow rates.

installed. Fructose is an isomerization product from glucose [18], and 5-HMF is a dehydration product from hexoses [19]. At lower temperatures, the depolymerization of starch barely proceeded, resulting in low glucose yields. The glucose yield increased with increasing reaction temperature up to 543 K (16.1% on carbon weight basis), but decreased at 563 K because of the further decomposition of glucose. Fructose and 5-HMF were not produced up to 493 K, and the yields gradually increased with increasing temperature. The maximum yields of fructose and 5-HMF were 3.1 and 5.1%, respectively, at the highest temperature, 563 K.

3.2. Effect of flow rate of hot water

The effect of the flow rate on the product distribution was studied by changing the values from 0.5 to 5 g/min at 513 K without a PFR installed. Fig. 4 shows the yields of the monosaccharides, the oligosaccharides and the aldehydes vs. flow rate. In this work, monosaccharides and aldehydes include glucose and fructose, and 5-HMF and furfural, respectively. Furfural is also a secondary product as well as 5-HMF although the yield was relatively low (<2%). The oligosaccharide yield was calculated as a difference between the yields of total WS saccharides and the glucose yield. As expected, the yield of oligosaccharides decreased and that of monosaccharides increased with decreasing the flow rate: lower flow rates resulted in the longer residence times in the reactor. The monosaccharide yield slightly decreased at the flow rate of 0.5 g/min. The maximum glucose yield was obtained to be 21.7% at 1 g/min. While the aldehyde yields were close to zero at 3 and 5 g/min, the production of aldehydes was accelerated at lower flow rates, or longer residence times.

GPC chromatograms of recovered solution obtained at different flow rates at 513 K are shown in Fig. 5. The MWD clearly shifted to smaller molecular weights as the flow rate decreased. This indicates that the degradation of starch was promoted at longer residence times in the reactor.

3.3. Effect of residence time of partially degraded and dissolved starch

The effect of the residence time of WS components eluted from the first reactor on the product distribution was investigated by installing a PFR downstream at the exit of the first reactor. Fig. 6 shows the product distribution at various residence times at (a) 513 K and (b) 493 K. In these figures, the yields of unknown substances are defined as the differences between the TOC values and the total carbon contents in the identified products. At 513 K and the residence time of 0 min in the PFR (corresponding to no installation of a PFR), oligosaccharides were the major products since the dissolved components were instantly eluted out of the first reactor and were immediately quenched. With increasing residence time, the oligosaccharides produced in the first reactor were further degraded hydrothermally in the PFR. As a result, the glucose yield was remarkably enhanced. Fructose and 1,6-anhydroglucose, which is a dehydration product from glucose, were slightly produced at the residence time of 1.82 min, and the yields did not change significantly at longer residence times. The yield of aldehydes, which are secondary degradation products, simply increased with residence time. At 493 K, shown in Fig. 6b, significant changes in yields of fructose, 1,6-anhydroglucose and aldehydes were not observed although oligosaccharides started decreasing and the glucose yield somewhat increased at residence times longer than 2 min. While the data were not shown, monosaccharides and aldehydes were scarcely produced and the oligosaccharide yields were almost unchanged around 90% at 453 and 473 K and residence times less than 6 min.

GPC chromatograms of recovered solutions at different residence times at 513 K are shown in Fig. 7. As the

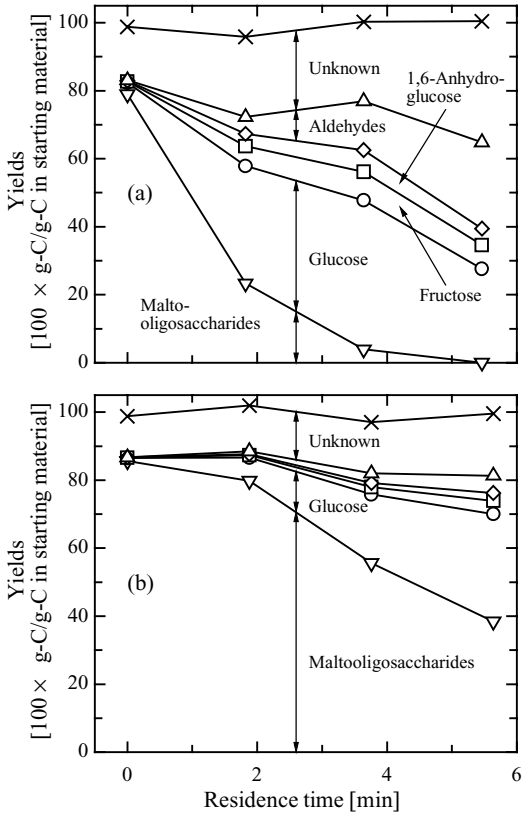

Figure 6 Product distribution at various residence times at (a) 513 K and (b) 493 K.

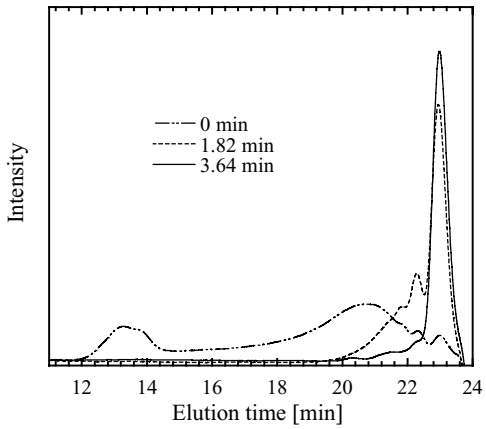

Figure 7 GPC chromatograms obtained at 513 K and different residence times.

effect of flow rate shown in Fig. 5, the MWD shifted to lower molecular weights with increasing residence time in the PFR. The peak of high molecular weight compounds around 13.5 min was diminished when the PFR was installed. These chromatograms indicate that the depolymerization of the partially degraded and dissolved starch in the first reactor significantly proceeded during the residence time in the PFR.

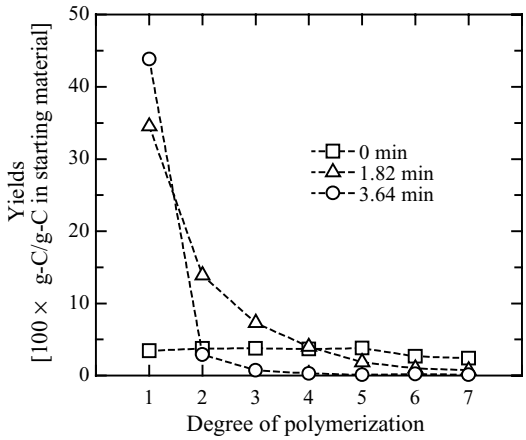

Figure 8 Yields of glucose and maltooligosaccharides with DP up to 7 obtained at 513 K and different residence times.

Fig. 8 shows the yields of glucose and maltooligosaccharides with DP up to 7 at various residence times at 513 K. In the absence of a PFR, all these saccharide yields were low and comparable to each other. By increasing the residence time to 1.82 min, the yields of saccharides with DP up to 3 increased, and those with DP larger than 4 decreased. At residence time of 3.64 min, the glucose yield was further increased to 43.8%, which is the highest glucose yield in this study, while the yields of maltooligosaccharides with DP larger than 2 were nearly zero. Such a tendency apparently indicates that glucose was produced by the break down of higher DP maltooligosaccharides.

3.4. Comparison of the effects of reaction temperature, flow rate and residence time

To compare the effects of reaction temperature, flow rate and residence time on the product distribution in the

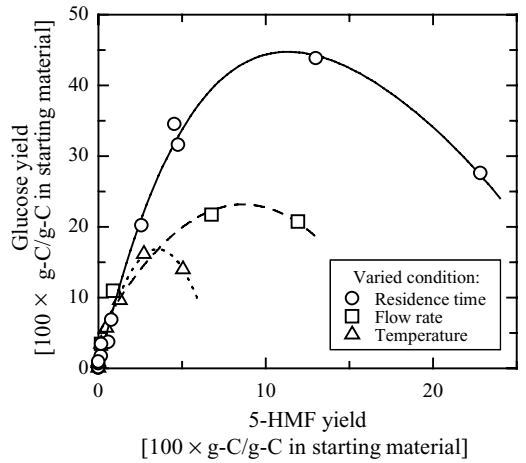

Figure 9 Glucose yield vs. 5-HMF yield obtained at various reaction temperature, flow rate of hot water and residence time of WS components.

hydrothermal degradation of starch, the glucose yield is plotted against the 5-HMF yield obtained by varying these three variables in Fig. 9. As mentioned above, since the 5-HMF yield simply increases with the reaction progress, 5-HMF is a measure indicating how intense the degradation reaction proceeds. The yield ratio of glucose to 5-HMF showed no remarkable difference at 5-HMF yields up to about 3% under all conditions. Above the value of 5-HMF yield, however, the glucose yields decreased or reached plateaus at higher reaction temperatures or lower flow rates, respectively. On the contrary, the glucose yield kept increasing and exceeded 40% by varying the residence time. Thus, the precise control of the residence time of WS components in the PFR was the most effective to promote the production and to suppress the decomposition of glucose.

4. Conclusions

The effects of three experimental variables, i.e., reaction temperature, flow rate of hot water and residence time of WS components, on the product distribution in the hydrothermal degradation of starch were studied by using a semi-batch reactor and a PFR connected in series. The major products were maltooligosaccharides, glucose and 5-HMF although small quantities of fructose, 1,6-anhydroglucose and furfural were also detected. The highest yield of glucose (43.8%) was obtained at 513 K, the flow rate of 5 g/min and the residence time in the PFR of 3.64 min. Precisely adjusting the residence time by installing a PFR at the exit of the first reactor was the most effective to achieve the high yield of glucose among the experimental variables.

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