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Decomposition Kinetics of Glucose and Fructose in Subcritical Water Containing Sodium Chloride

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Abstract: The kinetics of the decomposition and isomerization of glucose and fructose in pure water and water containing sodium chloride (1–20 % w/w) under subcritical conditions at 180–220 °C was investigated. The addition of sodium chloride in subcritical water accelerated the decrease of glucose, and the rate was expressed by the Weibull equation. Although the isomerization of glucose to fructose was observed in parallel with decomposition, the yield of fructose was lower at higher sodium chloride concentrations. Mannose was also formed from glucose with very low yield. It was seen that fructose decomposed much faster than glucose, in pure and salty subcritical water. The decomposition of fructose obeyed first-order kinetics in the initial stages of the reaction and could be expressed by the autocatalytic model in the later stages. The formation of glucose and mannose from fructose was not observed under any of the conditions investigated.

Key words: decomposition, kinetics, saccharide isomerization, sodium chloride, subcritical water

INTRODUCTION

The application of subcritical water treatment to food processing has gained attention in recent years. Subcritical water exhibits high reactivity due to its high ion product, and good extraction ability due to its low dielectric constant. By utilizing this extraction ability, many studies have been carried out to extract valuable substances such as oligo- and polysaccharides and phenolic compounds from food based biomasses.[1)2)3)4)5)6)] During treatment with subcritical water, several reactions related to the constituents occur along with the extraction. Since food consists of many substances, it is very difficult to analyze all the reactions taking place simultaneously. Therefore, the analysis has been performed in a simple model system containing a single component, to elucidate the reaction behavior. There are some studies dealing with the analysis for the conversion of fatty acid esters[7)8)] and dipeptides[9)10)] in subcritical water.

There are many reports dealing with the decomposition of saccharides, such as glucose, fructose, and maltose.[11)12)13)14)] It has been reported that glucose is isomerized to fructose and mannose by a base (OH⁻) in subcritical water, through the Lobry de Bruyn-Alberda van Ekenstein (LBAE) transformation in parallel with the direct decomposition of glucose.[14)15)] However, the yields of fructose and mannose were low, resulting in the low selectivity of these saccharides. We reported that the addition of alcohols such as ethanol and methanol, promoted the isomerization and selectivity during the subcritical treatment of glucose.[16)17)] Therefore, an additive in the subcritical water could change the reaction behavior, yield, and selectivity of fructose and mannose.

Salt (sodium chloride) is commonly used in food processing. It has been reported that the decomposition of saccharides, such as glucose, galactose, and cellobiose is accelerated in subcritical water containing salt (salty subcritical water).[18)19)] However, these reports are insufficient to understand the reactions related to the isomerization of saccharides in salty subcritical water. In this study, the decomposition and isomerization of glucose and fructose in salty subcritical water were investigated, and effect of the salt concentration on the decomposition rate of fructose was also evaluated.

MATERIALS AND METHODS

Materials. Glucose, fructose, sodium chloride, and DOWEX 50Wx8 cation exchange resin (50–100 mesh) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Other chemicals were purchased from Wako or Nacalai Tesque, Inc. (Kyoto, Japan).

Reactor. Subcritical treatment was carried out in a tubular reactor similar to a previous study.[17)] The tubular reactor consisted of an HPLC tube connected to an HPLC pump (LC-10ATVP, Shimadzu Co., Kyoto, Japan) and a back-pressure regulator (P-880, Upchurch Scientific, Inc., Oak

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Abbreviations: LBAE, Lobry de Bruyn-Alberda van Ekenstein; PEEK, poly ether-ether-ketone; HPLC, high performance liquid chromatography.

Harbor, USA). A part of the tube was immersed in a silicone oil bath (180−220 °C) for the treatment, and another part was placed in a water bath to terminate the reaction. Since aqueous solutions of sodium chloride are highly corrosive at high temperatures (180−220 °C), a stainless HPLC tube was considered unsuitable, and a 1/16-inch tube made of PEEK resin (poly ether-ether-ketone, 0.75 mm I.D. × 5 m) was used instead. Although the PEEK tube is inert, the pressure resistance at higher temperatures is not sufficient due to the glass transition of the PEEK resin. Therefore, to avoid breakage, the PEEK tube was inserted into a stainless tube (2 mm I.D. × 3 m), and the gap between the tubes was filled with silicone oil.

Subcritical treatment of glucose and fructose. Each saccharide was dissolved (1 % g/g-water) in distilled water or water containing sodium chloride (1−20 % g/g-water). Prior to the subcritical treatment, the solution was sonically degassed under reduced pressure, and a nitrogen gas bag was connected to the solution reservoir to prevent dissolution of atmospheric oxygen. The solution was then delivered into the tubular reactor at specific residence times (20−420 s), which were calculated based on the volume of the reactor (1.9 mL) and the specific volume of the sodium chloride solution.[20] The effluent from the reactor was collected and its saccharide composition was determined by HPLC. Prior to the HPLC analysis, the effluent (0.5 mL) was mixed with an equal amount of 1 % (w/v) xylose aqueous solution that was used as an internal standard, and the mixture was then mixed well with 1 mL of wet DOWEX 50Wx8 cation exchange resin (H$^+$ form) to remove sodium ions. The resulting supernatant was used for the HPLC analysis.

Analysis. Glucose, fructose, and mannose were determined at room temperature using an HPLC system with an SPD-20A UV-Vis detector (Shimadzu) at 190 nm and an LC-20AD pump (Shimadzu) connected to a COSMOSIL Sugar-D packed column (3.0 mm I.D. × 250 mm, Nacalai Tesque). The eluent was 80 % acetonitrile with a flow rate of 0.5 mL/min.

RESULTS AND DISCUSSION

Effect of temperature on the subcritical treatment of glucose and fructose.

Figure 1 shows the time courses for the decrease of glucose and the formation of fructose and mannose in subcritical water in the presence (1 %) or absence of sodium chloride at 180−220 °C. Hereafter, the term 'salt' will be used instead of sodium chloride unless otherwise specified. It was seen that while the decrease of glucose was slightly faster at 180 °C in salty subcritical water than in pure subcritical water, the difference was not significant. On the other hand, the presence of the salt obviously accelerated the decrease of glucose above 200 °C. These results indicate that the catalytic activity of sodium chloride toward the decrease was significantly enhanced above 200 °C.

The rate of formation of fructose increased at higher temperatures, while the presence of salt had a very small effect at 180 or 200 °C. However, salt accelerated the for-
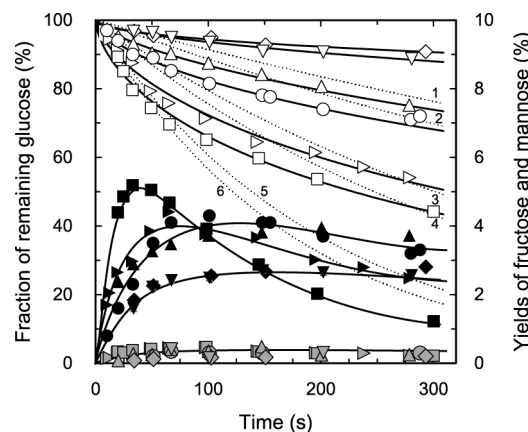
No.	Temp. (℃)	Salt conc. (%)	Glc	Fru	Man
1	180	0	◇	◆	◈
2	180	1	▽	▼	▽
3	200	0	△	▲	△
4	200	1	○	●	⬤
5	220	0	▷	▶	▷
6	220	1	□	■	▣

Fig. 1. Time courses for the fraction of remaining glucose and yields of fructose and mannose in the treatment of glucose at 180−220 °C, in the presence (1 %) or absence of sodium chloride.

Solid curves for the decrease of glucose represent the kinetically calculated results. Dotted curves are the calculated results assuming the first-order kinetics throughout the whole reaction. Numbers beside the dotted curves are the condition numbers listed in the symbol table. Curves for fructose and mannose formation are empirically drawn.

mation of fructose at 220 °C. The maximum yield of fructose reached approximately 5 % in salty subcritical water at 220 °C, indicating that the selectivity of fructose was higher. In addition, the decrease of fructose was observed in the later stage of the reaction at 200 or 220 °C, and the presence of salt accelerated the decrease at 220 °C.

The formation of mannose from glucose occurred with very low yield (< 0.5%), although it improved slightly at higher temperatures. We previously reported that approximately 3 % of mannose was formed during the subcritical treatment of glucose in aqueous alcohols.[17] Unlike the addition of alcohols, the addition of the salt did not promote the formation of mannose. From these results, the decrease of glucose would be mainly the combination of the isomerization and decomposition.

We also investigated the decrease of fructose, as it is one of the main products of the treatment of glucose, to analyze their mutual isomerization. Figure 2 shows the time courses for the decrease of fructose in the 180−220 °C range. The decrease of fructose was accelerated with increasing temperature both in pure and salty subcritical water. Also, the formation of glucose and mannose was not observed.

Thus, while the formation of fructose and mannose from glucose was observed (Fig. 1), the formation of glucose and mannose from fructose did not occur. Therefore, the decrease of fructose was only due to its decomposition, and the conversion from glucose to fructose can be considered
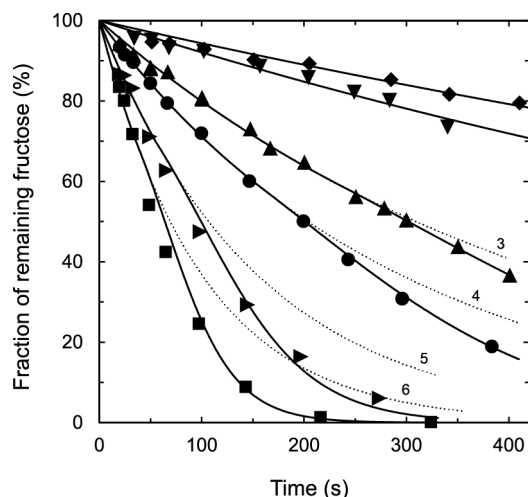
Fig. 2. Time courses for the decrease of fructose at 180−220 °C in the presence (1 %) or absence of sodium chloride.
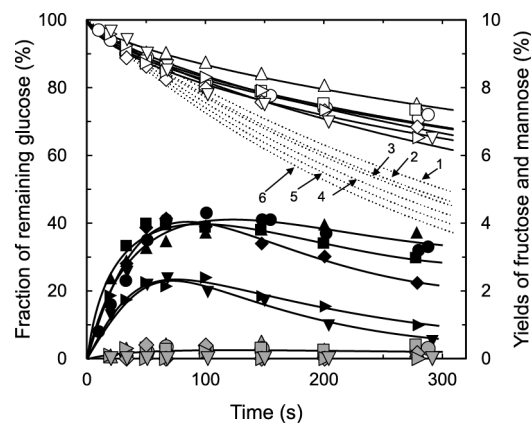   Numbers beside the dotted curves and symbols are the same as in Fig. 1.

irreversible in pure and salty subcritical water. This is in contrast to the observations in subcritical aqueous ethanol where glucose and mannose were formed to the extent of approximately 0.8 %.[17] Hence, the addition of salt was found to have a significant effect. The studies that follow were mainly carried out at 200 °C as the relatively slow re-action rates were suitable for reliable analyses.

Effect of salt concentration on the subcritical treatment of glucose and fructose.

The effect of salt concentration (0−20 %) on the decrease of glucose was investigated at 200 °C (Fig. 3). While the decrease of glucose was accelerated in salty subcritical wa-ter with increasing salt concentration, the degree of acceler-ation was small even at a concentration of 20 %.

On the other hand, the formation of fructose was signifi-cantly affected by the change in salt concentration. When the salt concentrations were low (0−5 %), fructose was formed at a maximum yield of approximately 4 % without any significant change in its formation rate. However, high-er salt concentrations (10−20 %) suppressed the formation of fructose, and the maximum yields were approximately 2 %. In all these cases, the decrease in the yield of fructose was observed at the later stages of the reaction due to its decomposition. These results would also indicate that the selectivity of fructose is low at higher salt concentrations, during the treatment of glucose. The yield of mannose was very low (< 0.5 %) at salt concentrations of 0−10 %, and was not observed at the highest salt concentration of 20 %.

Figure 4 shows effect of the salt concentration on the de-composition of fructose at 200 °C. Unlike glucose, the de-composition of fructose was greatly accelerated with in-creasing salt concentration, and sodium chloride itself acted as a catalyst.[21] The formation of glucose and mannose was not observed during the decomposition of fructose. These results indicate that the salt concentration affects the de-crease of glucose weakly and decomposition of fructose strongly. This effect also contributes to the lower yield of fructose in the treatment of glucose at higher salt concen-

Fig. 3. Time courses for the fraction of remaining glucose and yields of fructose and mannose in the treatment of glucose in subcritical water containing 0−20 % (g/g-water) sodium chloride at 200 °C.
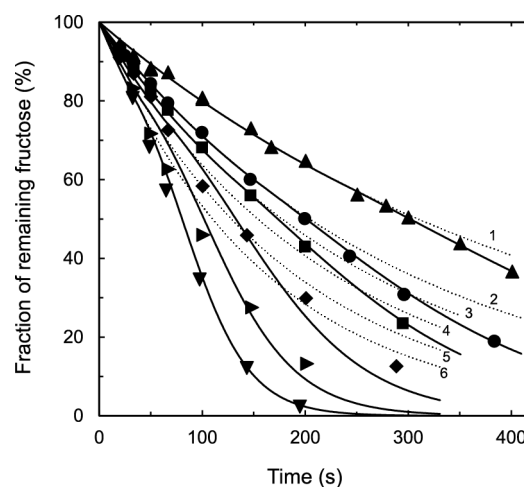   Numbers indicating the dotted curves are the condition numbers listed in the symbol table.

No.	Salt conc. (%)	Glc	Fru	Man
1	0	△	▲	△
2	1	○	●	●
3	2	□	■	■
4	5	◇	◆	◆
5	10	▷	▶	▷
6	20	▽	▼	▽

Fig. 4. Time courses for the decomposition of fructose in subcriti-cal water containing 0−20 % sodium chloride at 200 °C.
    Numbers beside the dotted curves and symbols are the same as in Fig. 3.

trations as shown in Fig. 3.

Kinetic analysis.

Kinetic analysis of the decrease of glucose and decompo-sition of fructose was performed in subcritical conditions to investigate the effects of the salt concentration. When the fractions of remaining glucose in Figs. 1 and 3 were plotted against time on a semi-logarithmic scale, straight lines were not obtained, and the reaction was found to decelerate at the later stages. Thus, the reaction could not be described by first-order kinetics. It was reported that the decrease of
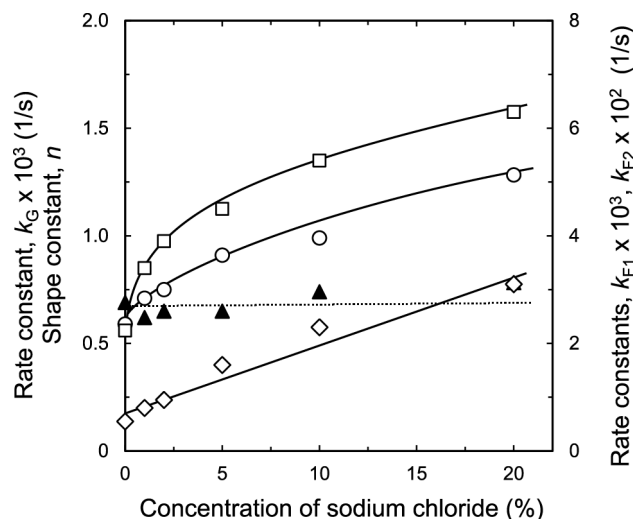
Fig. 5. Dependence of the rate and shape constants on the concentration of sodium chloride.
  The symbols, open circle, open square, open diamond, and closed triangle, represent k_G, k_{F1}, k_{F2}, and n, respectively.

Fig. 6. Arrhenius plot for the rate constant of each reaction.
  The symbols, circle, square, and diamond, represent the rate constants, k_G, k_{F1}, and k_{F2}, respectively. Open and closed symbols respectively represent the results in the presence (1 %) and absence of sodium chloride.

glucose in subcritical water can be empirically expressed by Weibull equation.[11)18)] Therefore, the Weibull equation (Eq. (1)) was also used to fit the time courses in the presence of salt:

$$C_G/C_{G0} = \exp\left[-(k_G t)^n\right] \tag{1},$$

where C_G is the concentration of glucose, C_{G0} is the initial glucose concentration, k_G is the rate constant of the decrease of glucose, t is time, and n is the shape constant. When $n = 1$, the reaction is first-order, and when $n < 1$, the equation gives a downward-convex curve.

  The k_G and n values at each condition were estimated by minimizing the sum of the residual squares between the calculated and experimental results using the Solver function of Microsoft® Excel 2013. The time courses of the decrease of glucose were expressed well by the Weibull equation at 180−220 °C with the salt concentration of 0 or 1 % (Fig. 1), and at all the salt concentrations at 200 °C (Fig. 3). The rate and shape constants were plotted against the salt concentration (Fig. 5). The shape constant, n, was approximately 0.7 and scarcely depended on the salt concentration. The rate constant, k_G, increased with increasing salt concentration, due to the catalytic activity of sodium chloride.

  The kinetic analysis of the decomposition of fructose at 180 °C revealed that the time courses could be expressed by the first-order kinetics (Eq. (2)) regardless of the presence of the salt (Fig. 2):

$$\frac{d(C_F/C_{F0})}{dt} = -k_{F1}(C_F/C_{F0}) \tag{2},$$

where C_F is the fructose concentration, C_{F0} is the initial fructose concentration, and k_{F1} is the rate constant for the first-order reaction. However, the first-order kinetics could be applied only at the early stages of the reaction at 200−220 °C with the salt concentration of 0 or 1 % (dotted curves in Fig. 2), and that at all the salt concentrations at 200 °C (dotted curves in Fig. 4), and the decomposition of fructose was accelerated at the later stages. The fraction of remaining fructose, when the first-order kinetics was not
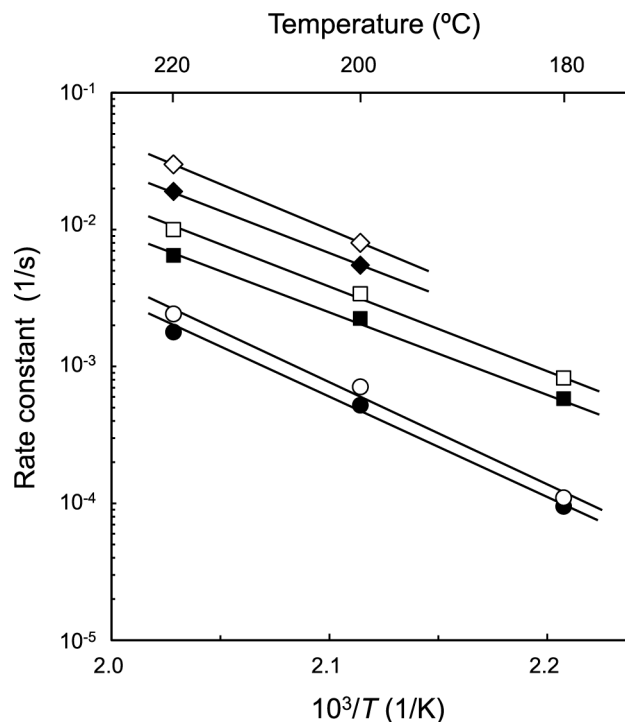
applicable, was approximately 60 % for lower salt concentrations (0−5 %) and approximately 80 % for higher salt concentrations (10−20 %). The difference in the fractions of remaining fructose was attributed to the catalytic activity of sodium chloride.

  It was reported that formation of organic acids such as formic acid, levulinic acid, and lactic acid occurs during the decomposition of fructose in subcritical water[13)14)15)] or under acidic conditions.[22)] In this study, organic acids could be formed during the decomposition, further promoting the decomposition of fructose in the later stages. Therefore, an autocatalytic reaction was assumed in the later stage:

$$\frac{d(C_F/C_{F0})}{dt} = -k_{F2}(C_F/C_{F0})(1 - C_F/C_{F0}) \tag{3},$$

where k_{F2} is a rate constant for the autocatalytic reaction. The calculated results coincided well with the experimental ones in the later stages, indicating that the assumption of an autocatalytic model is reasonable.

  Figure 5 shows the dependence of the rate constants, k_{F1} and k_{F2}, on the salt concentration. The values of k_{F1} and k_{F2} increased with increasing salt concentration, and k_{F2} showed a linear relationship with the salt concentration, C_S (%), as follows:

$$k_{F2}(1/s) = 1.27 \times 10^{-3} C_S + 7.45 \times 10^{-3}$$
$$(r^2 = 0.957) \tag{4},$$

showing the predictability of the rate constant, k_{F2}.

  All the obtained rate constants were plotted against the reciprocal of absolute temperature on a semi-logarithmic scale (Fig. 6, Arrhenius plot), and the plots yielded straight

lines with similar slopes. The activation energies ranged from 112 to 144 kJ/mol, similar to the results obtained for the decomposition of saccharides in other subcritical fluids[17] and ionic liquids,[23] and somewhat higher than in supercritical water.[24]

It has been suggested that glucose, fructose, and mannose mutually isomerize through the LBAE transformation in the presence of a base.[14)15] The treatment of glucose in this study yielded a small amount of fructose and mannose, indicating that glucose could be decomposed through the LBAE transformation in pure and salty subcritical water. On the other hand, in the decomposition of the fructose, the formation of glucose and mannose was not observed. The formation of organic acids through the decomposition of fructose would decrease the concentration of hydroxide ion, indicating that the acid-catalyzed decomposition would become dominant. Thus, the LBAE transformation requires alkaline conditions. This causes the suppression of glucose isomerization through the LBAE transformation in the later stages in the treatment of glucose, and also causes the suppression of the fructose isomerization to glucose and mannose.

In conclusion, the addition of sodium chloride in subcritical water accelerated the decrease of glucose and especially the decomposition of fructose. The decrease of glucose was described by the Weibull equation, while the decomposition of fructose obeyed first-order kinetics at the initial stages and was expressed by an autocatalytic equation in the later stage.

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