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Acid-Catalyzed Production of 5-Hydroxymethyl Furfural from D-Fructose in Subcritical Water

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A batch-type subcritical water system was used to perform the decomposition reaction of D-fructose to 5-hydroxymethyl furfural (HMF) over a temperature range of 473–593 K. The catalytic effect of various organic and inorganic acids with pH values in the range of 1.5–5 was evaluated. It was found that not only the pH, but also the nature of the acids, had great influence on the decomposition pathway. At lower pH, a rehydration of HMF to levulinic and formic acids occurred, whereas at higher pH, polymerization reactions occurred. Phosphoric acid (pH 2) was determined to give good balance between activity, yield, and byproduct amounts. The optimum condition for the best yield of HMF (65%) was achieved at a temperature of 513 K for a residence time of 120 s. The decomposition reaction of other monosaccharides and disaccharides were also investigated, and it was determined that the ketohexoses give higher yields than aldohexoses. However, all saccharides showed the possibility of the conversion to HMF in subcritical water.

1. Introduction

From an engineering viewpoint, subcritical and supercritical water have attracted growing attention in recent years as a promising chemical medium with a range of different applications, such as supercritical water oxidation of aqueous organic wastes,¹ subcritical water (hereafter called sub-CW) extraction,² and hydrolysis of organic compounds. Yoshida and co-workers^{3–6} have shown that sub-CW hydrolysis is an efficient method for the production of useful substances from fish wastes and other food-related substances. Recently, attention has been devoted to the hydrolysis and decomposition of biomass in sub-CW or supercritical water for the synthesis of industrial chemicals and related materials.^{7–13} More attention has been given to transforming saccharides into products with versatile industrial application profiles. In particular, because of diverse industrial applications of 5-hydroxymethyl furfural¹⁰ (hereafter called HMF), some investigators have performed dehydration of saccharides (and also from oligosaccharides and polysaccharides, which can yield hexoses on hydrolysis) into HMF in sub-CW.^{11–13} HMF is a versatile, polyfunctional compound, which is a potential building block for the synthesis of many types of polymers. For example, it is a good raw material for the synthesis of precursors of pharmaceuticals, themoresistant polymers, and macrocycles, particularly for the synthesis of dialdehydes, glycals, ethers, amino alcohols and acetals, and other organic intermediates that can lead to the production of numerous chemicals products such as solvents, surface-active agents, phytosanitary products, resins, and the like.^{10,14}

The synthesis of HMF has been known for many years.¹⁵ Scheme 1 shows a general type of the reaction: that is, an acid-induced elimination of 3 mol of water from saccharides occurs. The application of mineral acids (such as H₂SO₄, H₃PO₄, and

Scheme 1. Dehydration of Saccharides to 5-Hydroxymethyl Furfural (HMF)



HCl),^{16–18} organic acids (such as oxalic, levulinic, and *p*-toluenesulfonic acids (PTSAs),^{18–23} solid acids,^{23–25} transition-metal ions,^{26–28} and ion-exchange resins^{29,30} as the most commonly used catalysts have been reported. However, for sub-CW reactions, the application of acid catalysts mainly limited to inorganic acids.^{11–13} On the other hand, from the viewpoint of solvents used as reaction media, production methods generally can be divided into three main groups: reactions in water; reactions in organic solvents and/or organic–water mixtures; and, recently, reactions in sub-CW and supercritical water. In aqueous media, Neyret et al.³¹ have patented a method for the production of 28% of HMF from a solution of fructose containing NaH₂PO₄ and KHSO₄ at 403 K and 15 min. A 50% of production yield of HMF has been reported at 543 K and 12 s with NH₄Al(SO₄)₂ as the catalyst.³² Much lower yield (15.5%) has been obtained³³ via the hydrolysis of glucose in the presence of phosphoric acid at 463 K. The HMF yield can be increased by using organic solvents and/or an organic–water mixture.^{34,35} However, a high dilution system is required, compared to aqueous systems, because of low solubility of saccharides. This problem have been resolved with the application of organic–water mixture.³⁶

Recently, many scientists prefer water, which is the most popular benign green solvent, instead of using traditional toxic organic solvents or their mixtures with water for chemical reactions. Water at its critical status has properties that are different from water under normal conditions. An example is the low relative dielectric constant, which is comparable with that of methanol or acetone under ambient conditions. Because of these properties, along with the higher concentration of

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hydrogen and hydroxide ions,⁷ it seems to be a good alternative medium.³⁷ A few studies on the production of HMF in the sub-CW have been reported: in the presence of H_2SO_4 as a catalyst,¹¹ at 523 K, the combined yield of 60% was obtained for HMF and furfural. Antal et al.¹² have studied the mechanism of dehydration of fructose at sub-CW at 523 K, and they have reported yields of 47% and 53% for HMF in the absence and presence of H_2SO_4 as the catalyst, respectively. The application of an acetone–water mixture at its subcritical and supercritical status has also been reported,¹³ and the maximum yield of 78% was obtained at 453 K with H_2SO_4 in an acetone–water mixture (9:1).

Although, in the traditional techniques for production of HMF, the effects of various solvents and catalysts on reaction yield have been studied, the comparison of different catalysts and especially the effect of pH on reaction pathway and products in sub-CW systems have not been studied yet. In this paper, we used sub-CW as reaction media for the decomposition of fructose to make a comparative study between different organic and inorganic acids with a variety of initial pH values of the solution, to obtain the higher yield of HMF from saccharide feedstocks.

2. Experimental Section

2.1. Starting Materials. D-(–)erythrose was obtained from Acrose Organics (USA); dihydroxyacetone, glycolaldehyde, and pyruvaldehyde were obtained from Biomedicals, Inc. (Germany). All other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

2.2. Procedure. The reactor used for sub-CW treatment was constructed from a stainless steel tube (SUS316 with an inner diameter (id) of 8 mm and a total volume of 7.7 cm³) and a Swagelok fitting (readymade, from Swagelok AG, Switzerland). In a typical experiment, fructose (~50 mg) and water or a buffered aqueous solution (4.5–6 g) was placed into the reactor. Argon gas was used as a purge gas, to force out air in the reactor before the reaction, and then the reactor was capped tightly. It was immersed in a salt bath (Thomas Kagaku Co., Ltd.) that was preheated to the desired reaction temperature; sub-CW reaction was allowed to proceed for a given residence time. The reactor was then removed from the salt bath and quickly quenched by immersion into a water bath at room temperature. The pressure inside the reactor during the reaction was estimated from a steam table;⁶ the pressure inside the reactor was determined to be 1.55 MPa at 473 K and increased to 11.28 MPa at 593 K.

2.3. Analysis. After sub-CW reaction, the sample was diluted to 50 cm³ with distilled water and analyzed for HMF, fructose, and other byproducts. A CSPAK Narrow-bore column C18 (2.1 × 100 mm) in a high-performance liquid chromatography (HPLC) apparatus, using two Varian ProStar 210 solvent delivery modules coupled with electrospray ionization mass spectrometry (ESI–Varian 1200 Quadrupole MS/MS) and/or a photodiode array (PDA) detector (Varian PDA 330 Detector) was used for identification and quantitative analysis of the products. The absorbance of the detector for HMF and furfural was set to 284 nm.

The concentrations of organic acids were determined via HPLC, using a Shimadzu model LC-10AD VP pump with two serial ion-exclusion chromatography columns (Shim-pack model SCR-102H, 8 mm × 300 mm) and post-column pH-buffered electroconductivity detection (Shimadzu model CDD-6A). The mobile phase was 5 mM *p*-toluenesulfonic acid (hereafter called PTSA) solution at a flow rate of 0.8 mL/min. A mixture of 5

mM of PTSA and 100 mM of EDTA was used as a post-column reagent at a flow rate of 0.8 mL/min. The column temperature was kept at 313 K.

Two serial size-exclusion chromatography columns (Shodex-sugar models KS 804 and KS801, 8 mm × 300 mm) in a HPLC system, using a Jasco PU-2080 plus pump coupled with a refractive index detector (RI 2031 plus), were used for quantitative analysis of the products that could not be detected by an ultraviolet (UV) detector. The HPLC apparatus was operated at an oven temperature of 303 K, and water (at a flow rate of 0.4 mL/min) was used as the mobile phase. The total organic carbon (TOC) concentration of samples was measured using a TOC analyzer (Shimadzu model TOC-500). CHNS analysis (Perkin–Elmer, model 2400) was used to calculate the carbon and hydrogen content of the solid product. The pH of solutions was measured using glass pH-electrode that was attached to Horiba pH/ion meter f-23 equipment. A double-beam UV-visible spectrophotometer (Shimadzu, model UV-160A) was used for spectrophotometric measurements. Elemental analysis was performed using inductively coupled plasma–atomic emission spectrophotometry (ICP-AES) (model SPS-7800 plasma spectrometer, Seiko, Japan). The composition of the aqueous phase after sub-CW reaction was diluted to 25 mL, and the cations were directly determined using ICP equipment.

3. Results and Discussion

3.1. Uncatalyzed Reactions—Influence of Temperature and Residence Time. Decomposition reactions of fructose in sub-CW were evaluated without acid catalysts by varying the parameters of temperature and residence time. All major and minor products that were identified from the sub-CW decomposition of fructose are listed in Table 1.

Scheme 2 shows the general reaction pathways for the decomposition of fructose under sub-CW conditions that have been reported by several researchers. Pathways [a] and [b] show the dehydration of fructose to HMF and, consequently, rehydration of HMF to levulinic and formic acids.¹¹ Apart from HMF, traces of many other dehydration products such as polymeric side reactions (humin) and furfural are formed (pathways [c], [d], and [e]).^{11,12,38}

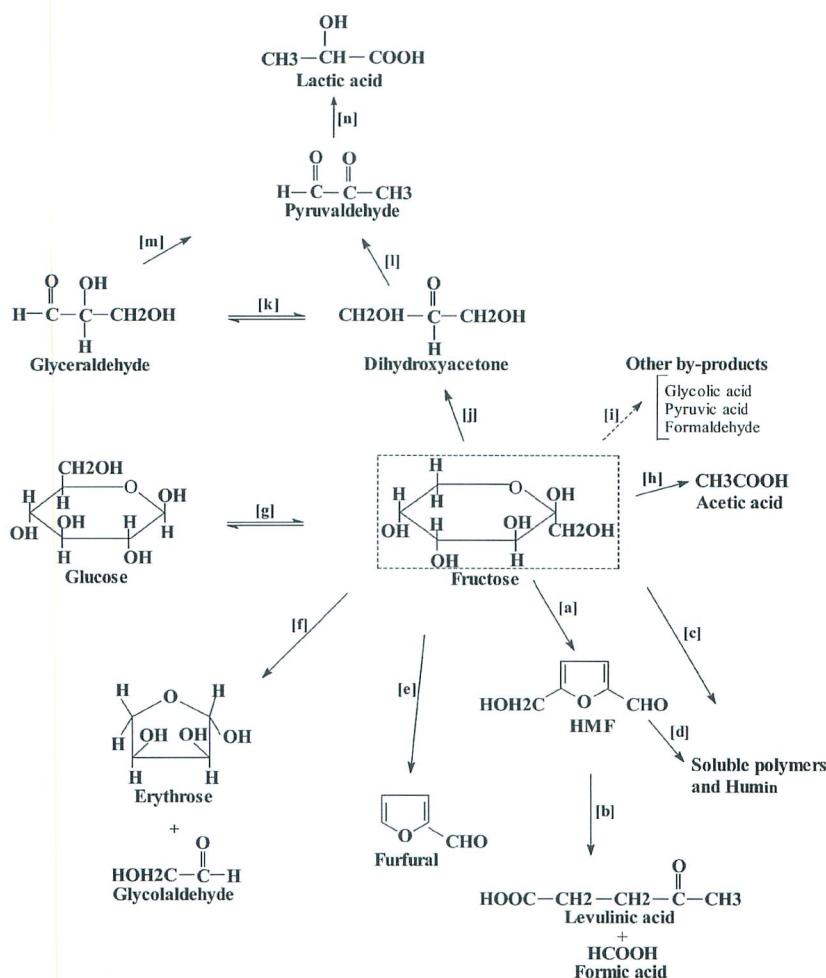
Pathways [g] and [f] in Scheme 2 were reported by Kabyemela et al.,³⁹ in which fructose can be isomerized by ring opening to glucose. In addition, erythrose and glycolaldehyde may be formed by reverse aldol condensation reactions of fructose and/or glucose in their acyclic forms. Using glucose as a substrate, the formation of the C-3 carbon compounds glyceraldehyde and dihydroxyacetone has also been reported by Kabyemela et al.⁴⁰ (see pathways [j] and [k]). Furthermore, using fructose as a substrate, we identified the same decomposition products.

The reversible isomerization between glyceraldehyde and dihydroxyacetone (pathway [k]) and their sequence dehydration to pyruvaldehyde (pathways [l] and [m]) have been studied in water at high temperature.⁴¹ Under the same conditions, it has been identified as benzilic rearrangement of pyruvaldehyde to lactic acid (pathway [n]). Pathway [h], the formation of acetic acid, has been identified from the decomposition of glucose in supercritical water.³⁸ Formaldehyde, pyruvic acid, and glycolic acid (pathway [i]) have been identified in this study.

Scheme 2 is the combination of pathways that were proposed by the different researchers individually, as mentioned previously. In this work, we determined that all the pathways should be considered in the decomposition reaction of fructose in sub-CW.

Figure 1 shows the effect of sub-CW temperature on the decomposition of fructose at a residence time of 120 s; for

Scheme 2. Decomposition Pathway of Fructose under Subcritical Water (Sub-CW) Conditions with and/or without Acid Catalysts^a



^a Pathways a–b–c–d–e are taken from refs 11, 12, and 38; pathways g and f are taken from ref 39; pathways j and k are taken from ref 40; pathways k–l–m–n are taken from ref 41; pathway h is taken from ref 38; and formaldehyde, pyruvic acid, and glycolic acid have been identified in this study.

Table 1. Identified Products from Sub-CW Decomposition of Fructose in the Temperature Range of 473–593 K and Residence Times up to 900 s

Furan Derivatives and Polymers		Aldehydes, Ketones, and Monosaccharides		Organic Acids	
ID	product	ID	product	ID	product
1	HMF	5	glucose	12	pyruvic acid
2	furfural	6	glyceraldehyde	13	glycolic acid
3	soluble polymers	7	glycolaldehyde	14	lactic acid
4	humin	8	erythrose	15	formic acid
		9	formaldehyde	16	acetic acid
		10	pyruvaldehyde	17	levulinic acid
		11	dihydroxyacetone		

simplicity, we divided the products into three groups: HMF, furfural, and remained fructose (Figure 1a); aldehydes, ketones, and monosaccharides (Figure 1b); and organic acids (Figure 1c). The absolute yield of component *i* was defined by eq 1.

$$[\text{absolute yield (\%)}]_i = C_i (\text{g}/100 \text{ g of initial reactant}) \times \frac{\text{MW of reactant}}{\text{MW of } C_i} \quad (1)$$

The temperature has a strong influence on the reaction, from low to moderate temperature (i.e., 473–533 K), as indicated by the decomposition of fructose (not only is HMF the main

product, but also some other byproducts were produced; see Figure 1); however, at temperatures higher than ~533 K, the production yield decreases, because of decomposition and polymerization reactions of both reactant and HMF, similar to what is reported under normal conditions.⁴² The shape of the yield–temperature curve of furfural produced mainly from the decomposition of fructose is similar to HMF, although the amount is smaller than that of HMF (see Figure 1a). The yield of minor products, including four aldehydes (formaldehyde, pyruvaldehyde, glyceraldehyde, and glycolaldehyde), one ketone (dihydroxyacetone), and two monosaccharides (glucose and erythrose) was indicated by peaks at temperatures in the range of 513–533 K (Figure 1b). Because, from Figure 1b, it can be found that the isomerization of fructose to a small amount of glucose can occur under sub-CW conditions, it is reasonable to assume that the glucose produced is also dehydrated to HMF. The yield of organic acids (lactic, formic, acetic, glycolic, pyruvic, and levulinic acids), which were the second group of minor byproducts, increased with temperature, and the lactic acid and formic acids showed higher yields than all other organic acids (Figure 1c).

Figure 2 shows the time course of the decomposition of fructose without catalysts in the sub-CW at 513 K. Fructose decomposed quickly within 300 s, and the yield of HMF increased up to 200 s. Thereafter, the yield of HMF decreased

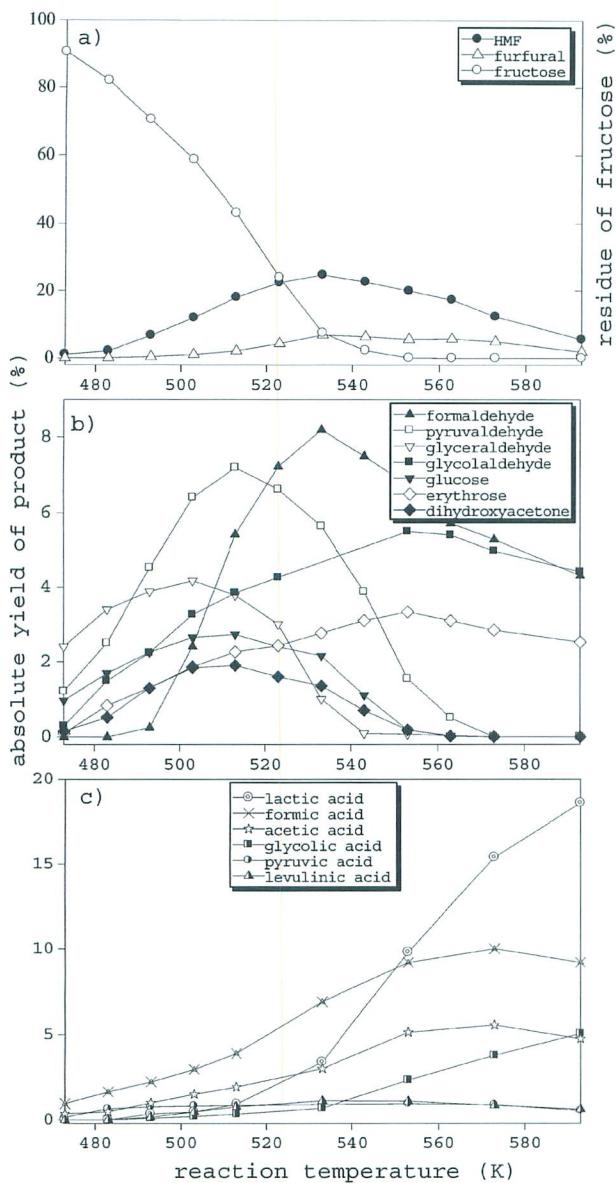


Figure 1. Effect of temperature on product yields of fructose decomposition without catalyst for a residence time of 120 s and an initial fructose concentration of 0.05 M.

due to the polymerization and decomposition reactions. Figure 2b and c shows the yield of the byproducts. The byproducts given in Figure 2b showed peaks at ~ 150 – 200 s. On the other hand, the yield of organic acids increased with time (see Figure 2c).

As our experimental results show, sub-CW has potential to decompose the fructose to HMF. However, in the absence of an acid catalyst, a relatively low dehydration yield of fructose to HMF was observed, because of side reactions. Generally, one of the main side reactions under normal conditions is a secondary reaction involving the rehydration of HMF to levulinic and formic acids³⁴ (see Scheme 2); usually, in aqueous media, the rehydration of HMF under normal conditions becomes an important subsequent reaction²² (but not in organic solvents). In Figures 1c and 2c, it can be concluded that, in sub-CW, the rehydration of HMF is relatively low. This is because the dielectric constant of sub-CW is close or similar to that of organic solvents. Another main side-reaction is polym-

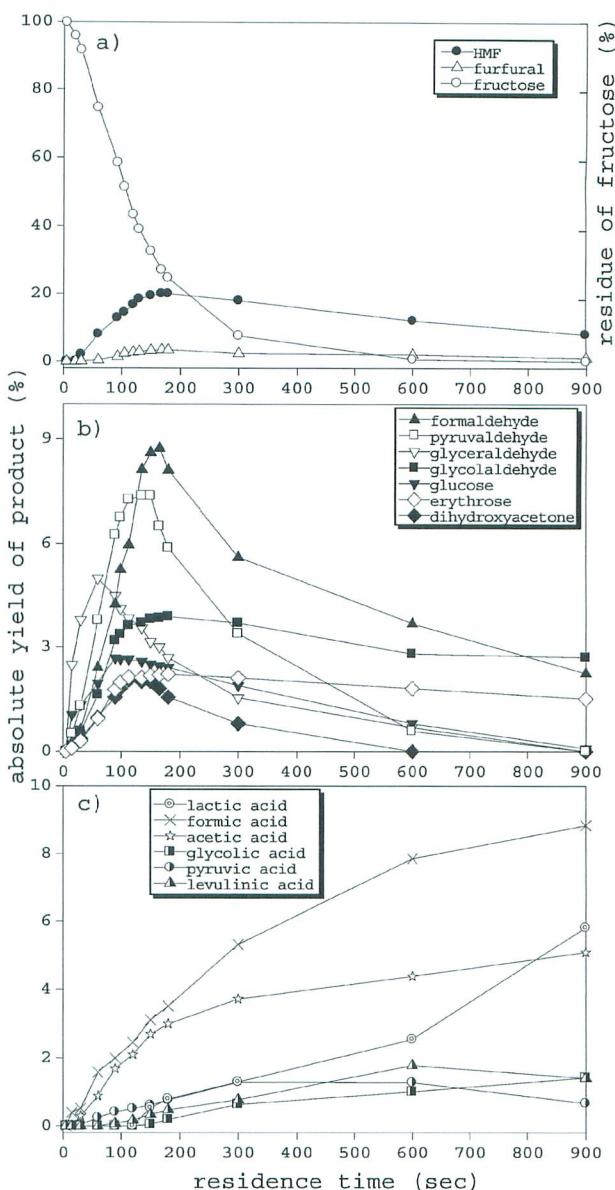


Figure 2. Time course of product yields of fructose decomposition without catalyst at 513 K and an initial fructose concentration of 0.05 M.

erization of fructose and/or HMF in both normal⁴³ and sub-CW conditions.¹² The aqueous solution of fructose after sub-CW treatment became brown, which was ascribed to the formation of soluble polymers. Because of the solubility of these compounds, they seem to have a lower degree of polymerization. However, as the temperature, residence time, or initial concentration of reactant increased, the soluble polymers changed to solid forms. The ratio of absorbance of the solution at 350, 400, and 450 nm corresponded to the concentration of soluble polymers which in all experiments were determined to be 5:1.9:1. These results were similar to those obtained from the reactions of fructose under normal conditions.⁴⁴

The absorbance of the aqueous solution, as a function of sub-CW temperature, is shown in Figure 3. Depending on the reaction conditions, the polymers may be in soluble or solid forms. To avoid producing solid humin, a low initial concentration of fructose (0.05 M) was used in this study. The coloration had a tendency to increase as the temperature increased and, consequently, the concentration of HMF and fructose decreased

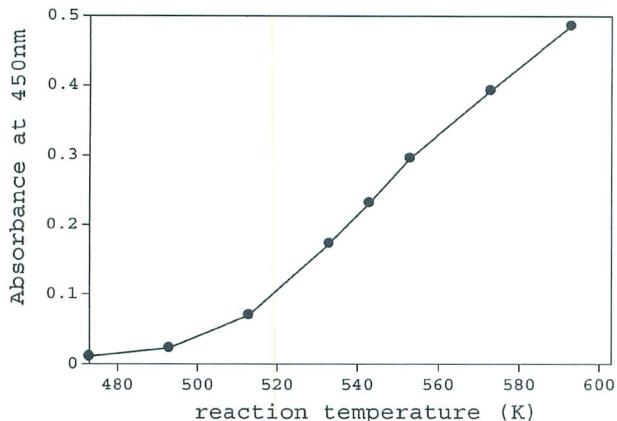


Figure 3. Absorbance of the decomposition solution of 0.05 M fructose without catalyst, as a function of the subcritical water (sub-CW) temperature for a residence time of 120 s.

(see Figure 1a). The overall carbon balance showed no deficit (except in the case of the formation of solid humin) and account for >99% of the initial amount of carbon. In the reactor, there is a water-vapor phase and an aqueous-solution phase. The sub-CW reaction occurs in the aqueous-solution phase. No inorganic carbon was detected in any of the experiments.

After the sub-CW reaction, the pH of the solution changed from neutral to acidic values ($\text{pH} \sim 3.5$), because of the formation of acidic products, which led to the conclusion that, similar to normal conditions,⁴⁵ autocatalysis may occur during sub-CW decomposition reaction. However, in the uncatalyzed reactions, the amount of organic acids produced (consequently, the pH of the solution during reaction), along with protons from the ionization of water at its critical status, does not seem to be sufficient to catalyze the reaction to obtain a higher yield of HMF.

3.2. Acid-Catalyzed Reactions—Influence of Acid Type and pH. In this study, hydrochloric, sulfuric, phosphoric, oxalic, citric, maleic, and *p*-toluenesulfonic acids that have previously been used to decompose saccharides under normal temperature and pressure conditions were selected as the common homogeneous acids, for evaluation of their applicability to the dehydration of fructose in sub-CW. Because of our interest in the formation of the HMF, we emphasize studies in acidic conditions. An initial concentration of 0.05 M fructose and 0.1 M of each acid was used in pH range of 1.5–5; however, for HCl and H_2SO_4 , which do not have buffering properties (strong acids), a sufficient amount of acids was used to obtain desired pH (1.5 to 4). Because it was impossible to determine the pH of the solution during sub-CW reaction, we measured only the initial and final pH values of the solutions under ambient conditions. The reactions were performed at 513 K for a residence time of 120 s. The results of decomposition products of fructose for each initial pH are summarized in Table 2, in sections labeled (a)–(f). The results of an uncatalyzed reaction are also given. Similar to the uncatalytic reactions, some byproducts and remained fructose were also identified in the catalytic reactions. As mentioned previously, the yield of HMF in the uncatalyzed reactions does not exceed more than 23% (at 533 K for a residence time of 135–150 s). The results of the catalytic reactions showed that a higher yield of HMF could be generally obtained at pH values in the range of 2–2.5.

(1) At pH 2, the phosphoric acid catalyst, gave the highest yield of HMF among all acid catalysts used in this study. Under more-acidic conditions ($\text{pH} < 2$), rehydration of HMF to levulinic and formic acids increased. Increasing pH toward 5,

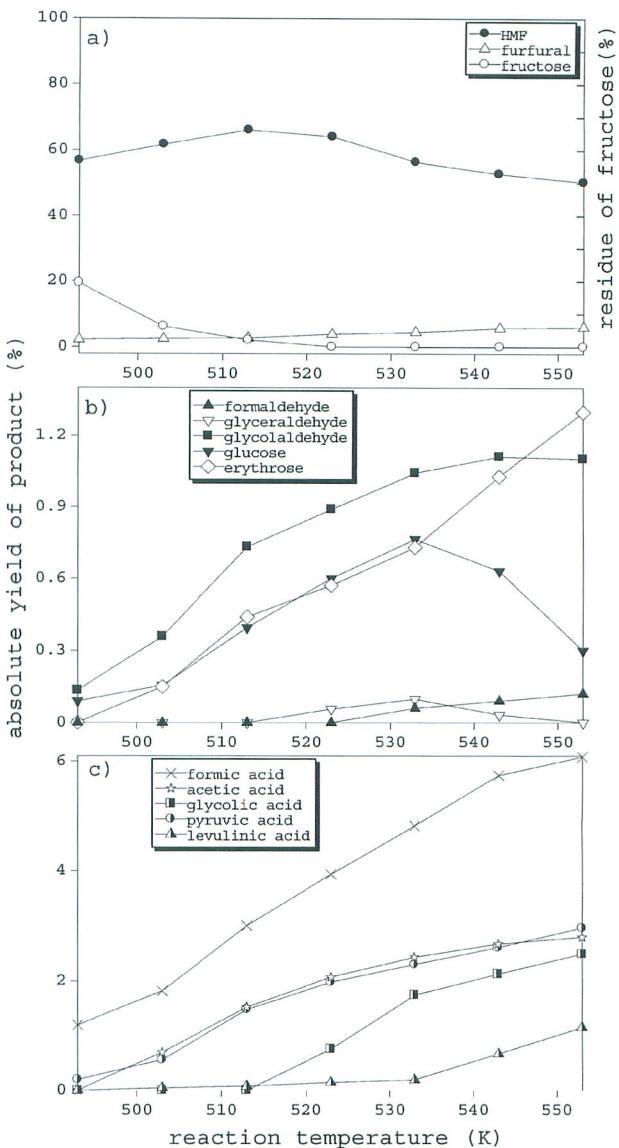


Figure 4. Product yields of fructose decomposition with phosphoric acid (pH 2) as a catalyst for a residence time of 120 s and an initial fructose concentration of 0.05 M, as a function of the sub-CW temperature.

the yield of HMF decreased, and the lowest yield was obtained at pH 5. The amount of byproducts produced varied with pH (see Table 2). Although >95% of the fructose decomposed within the entire range of the experimental pH, at higher pH, the yield of HMF decreased and the concentration of byproducts did not exhibit a big variation in the pH range. These results led us to conclude that, at higher pH values, fructose and/or HMF were oligomerized or polymerized to give soluble polymeric byproducts (similar to what has been already reported under normal conditions⁴²). It has been already shown⁴⁶ that the rehydration of HMF under normal conditions give equimolar amount of levulinic and formic acids. However in the case of sub-CW reaction, we showed that the equimolarity of these two components was no longer maintained. By increasing pH, the yield of formic acid increased, whereas no levulinic acid was detected. On the other hand, parallel to increasing the yield of formic acid, the yields of other organic acids (pyruvic and acetic acids) increased. It seems that formic acid and other organic acids were directly produced from the decomposition of fructose.

(2) The catalytic behavior of maleic acid in the formation of

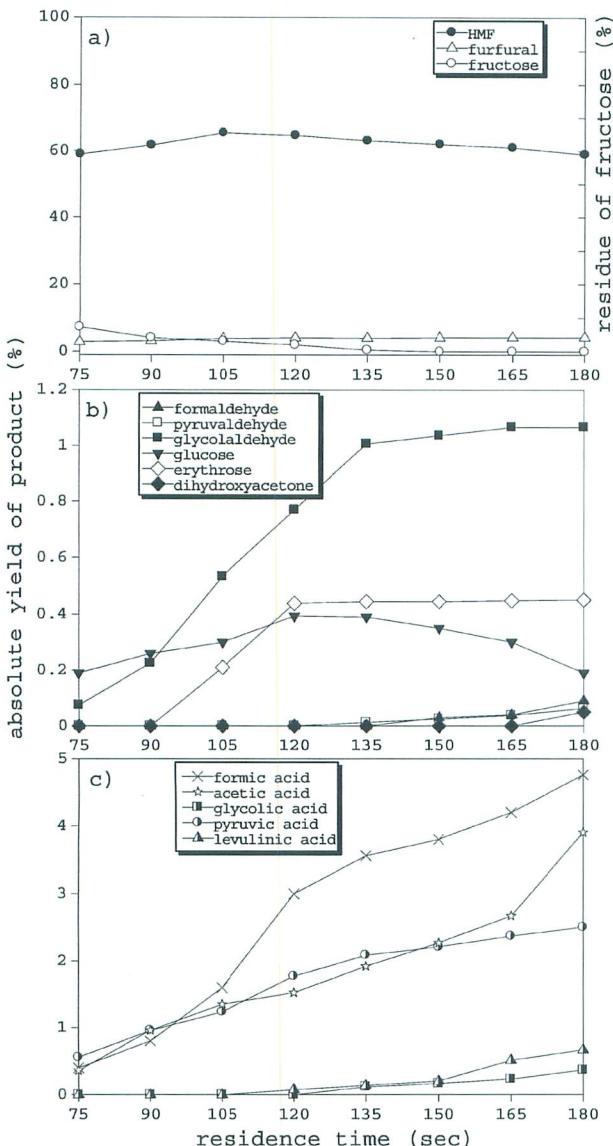


Figure 5. Product yields of fructose decomposition with phosphoric acid (pH 2) as catalyst at 513 K and an initial fructose concentration of 0.05 M, as a function of residence time.

HMF was similar to that of phosphoric acid. The yield of HMF showed a peak at pH \sim 2 (60%). In more-acidic media (pH 1.5), the rehydration of HMF to levulinic and formic acids was observed. However, the amount of levulinic acid was greater than that of formic acid. At higher pH values (i.e., pH $>$ 4), a small amount of other organic acids, which were much smaller than for the case in phosphoric acid, were identified.

(3) In PTSA, at pH 2, a relatively high yield of HMF (\sim 37%) was obtained (Table 2b). Under more-acidic conditions, HMF was rehydrated to almost equimolar amounts of levulinic and formic acids. Up to pH 2.5, $>99\%$ of the fructose was decomposed, whereas at pH 3, the highest stability of fructose was observed. At pH $>$ 3, by increasing pH, the conversion of fructose to soluble polymers increased with an increase in pH. Relatively large amounts of pyruvaldehyde and glyceraldehyde at higher pH values can be obtained using this acid.

(4) Citric acid and oxalic acid showed different catalytic behavior from the other acids. In these catalysts, the higher HMF yield was obtained at pH 1.5 and the yield decreased sharply as the pH increased toward a value of 5. Interesting results were

obtained in the conversion of fructose: that is, at pH 1.5, \sim 3.5% and \sim 5.8% fructose were identified to be present in the citric acid and oxalic acid, respectively. On the other hand, at pH $>$ 1.5, no fructose remained; in regard to rehydration products, only formic acid was observed. This result shows again the possibility of another pathway in the production of formic acid apart from the dehydration of HMF. Significant amounts of organic acids, along with other byproducts, were identified. Their concentrations varied with pH (see Table 2). Despite the application of the citric acid and oxalic acid as suitable acid catalysts under normal temperature and pressure reactions,^{18–23} it seems that, in sub-CW, reactions of fructose in the presence of these acid catalysts have a tendency toward polymerization more than toward the formation of HMF.

(5) In HCl, the maximum HMF yield was obtained at pH 2.5. In H₂SO₄, it was produced within the pH range of 2–2.5. An interesting behavior was observed for the rehydration of HMF with HCl. Starting with HCl at pH 1.5, a maximum rehydration yield of HMF was shown among all acids (\sim 46.1% and \sim 50.7% for levulinic and formic acids, respectively), whereas with H₂SO₄, the amount of levulinic and formic acids produced was less than that in HCl (see Table 2a). The rehydration reaction yields may be improved through optimization of the reaction, which has not been attempted in this study. In these two acid catalysts, by increasing the pH from 1.5 toward 5, the amount of unreacted fructose increased, compared to other acid catalysts. It can be attributed to the incapability of HCl and H₂SO₄ to maintain a constant pH, especially at lower concentrations (or higher pH). Therefore, similar to uncatalyzed reactions, the produced organic acid during the reaction may control the pH of sub-CW solution. Although HCl and H₂SO₄ are both strong acids, they showed different catalytic behaviors, especially in low pH; at pH 1.5, the yield of HMF with H₂SO₄ is \sim 2 times larger than that with HCl, whereas a greater amount of rehydration products was obtained with HCl than with H₂SO₄. Tyrlík et al.⁴⁷ have studied the catalytic effects of MgCl₂ and MgSO₄ in aqueous solution on the dehydration of saccharides in a conventional system at normal temperature and pressure, and they found different effects from anions of these salts on the reactivity of monosaccharides. To see the effect of the anions of these two acids on decomposition of fructose in sub-CW, a series of experiments was conducted at pH 1.5 with HCl and H₂SO₄, respectively, and with a mixture of Na₂SO₄ and NaCl (Table 3). The experimental results in entries a and b of Table 3 show that the catalytic effect of HCl was higher than that of H₂SO₄ in the rehydration reaction of HMF to levulinic and formic acids. On the other hand, by adding Na₂SO₄ to the HCl solution (entry c), the rehydration reaction greatly decreased and, consequently, the yield of HMF increased from \sim 9% to 23%. By adding NaCl to the H₂SO₄ solution (entry d), the rehydration reaction increased and the HMF yield remained almost the same as that observed for entry b. The results of the experiment for entry e, in which a 1:1 mixture (v/v) of HCl and H₂SO₄ was used, were almost an average of the results of entries a and b. These series of experiments led us to the following tentative conclusions: (i) Cl⁻ ions can accelerate the conversion of fructose to HMF and, consequently, HMF to rehydration products; (ii) sulfate ions have an inhibitor effect on the rehydration reaction; and (iii) the absorbance results of solutions at three wavelengths (350, 400, and 450 nm), which corresponds to the concentration of soluble polymers, shows that polymerization products with HCl are lower than H₂SO₄.

The aforementioned results show the importance of the effect of acids and pH on the decomposition of fructose. Generally,

Table 2. Comparison Series of Organic and Inorganic Acid-Catalyzed Decomposition of 0.05 M Fructose, Conducted in the pH Range of 1.5–5 at 513 K and a Residence Time of 120 s, as a Function of the Absolute Yield of Reactant and Products^a

products	HCl	H ₂ SO ₄	H ₃ PO ₄	citric acid	maleic acid	PTSA	oxalic acid	uncatalyzed
(a) pH 1.5								
HMF	9.01	28.45	55.95	49.30	40.21	9.87	18.20	18.08
furfural	4.08	2.13	5.08	3.32	7.24	3.66	0.65	2.14
fructose	ND	0.22	0.35	3.47	0.22	0.17	5.88	43.06
glucose	ND	0.21	0.27	0.39	0.20	0.15	1.52	2.70
glyceraldehyde	ND	0.48	ND	ND	ND	ND	1.40	3.78
glycolaldehyde	ND	2.33	0.48	4.31	0.72	0.77	6.87	3.70
erythrose	ND	ND	ND	1.27	0.19	0.21	1.65	2.11
formaldehyde	ND	0.70	ND	ND	0.27	ND	6.44	5.70
pyruvaldehyde	ND	ND	ND	ND	ND	ND	2.37	7.25
dihydroxyacetone	ND	1.30	ND	1.22	ND	ND	1.96	1.99
pyruvic acid	1.15	0.66	0.89	1.41	1.34	0.75	1.26	0.82
glycolic acid	0.10	ND	ND	1.26	ND	ND	1.12	0.14
lactic acid	5.05	9.39	ND	1.83	ND	0.18	2.09	0.91
formic acid	50.68	23.12	13.36	11.67	8.86	49.04	11.92	0.90
acetic acid	1.10	1.08	1.22	ND	ND	1.12	1.44	0.64
levulinic acid	46.08	17.50	7.01	ND	10.98	33.72	ND	0.10
(b) pH 2								
HMF	29.59	40.31	65.30	17.55	60.03	37.01	17.40	18.08
furfural	4.32	2.99	3.90	1.12	6.41	4.84	0.50	2.14
fructose	0.41	1.42	2.08	0.10	6.07	0.28	2.49	43.06
glucose	0.82	0.13	0.39	0.04	0.88	0.27	0.80	2.70
glyceraldehyde	0.86	2.00	ND	ND	0.30	ND	1.30	3.78
glycolaldehyde	3.36	3.12	0.73	9.2	1.38	1.47	11.95	3.70
erythrose	ND	ND	0.45	3.00	0.39	0.39	4.38	2.11
formaldehyde	0.53	6.32	ND	ND	7.59	0.15	7.33	5.70
pyruvaldehyde	3.45	1.87	ND	ND	1.57	0.39	0.25	7.25
dihydroxyacetone	ND	0.58	ND	ND	ND	ND	1.55	1.99
pyruvic acid	2.11	1.28	1.40	2.49	0.97	0.60	2.77	0.82
glycolic acid	0.30	ND	ND	5.00	ND	ND	5.40	0.14
lactic acid	5.69	4.19	ND	2.69	ND	0.43	2.97	0.91
formic acid	27.22	14.46	3.06	12.32	2.92	26.16	14.86	0.90
acetic acid	1.07	0.96	1.72	1.79	ND	0.98	6.00	0.64
levulinic acid	21.60	14.62	ND	ND	ND	21.25	ND	0.10
(c) pH 2.5								
HMF	44.74	40.57	52.72	7.94	51.20	28.80	8.10	18.08
furfural	2.84	2.72	3.49	0.51	5.67	2.05	1.25	2.14
fructose	2.04	10.27	3.85	ND	20.67	0.81	1.09	43.06
glucose	1.43	1.35	1.38	ND	1.46	0.79	0.50	2.70
glyceraldehyde	2.75	3.53	ND	ND	3.22	0.82	1.21	3.78
glycolaldehyde	4.40	3.88	2.74	9.80	3.31	2.70	12.65	3.70
erythrose	1.11	0.85	0.61	3.51	0.90	0.45	4.80	2.11
formaldehyde	1.25	7.46	ND	ND	5.84	3.37	0.18	5.70
pyruvaldehyde	16.75	5.90	1.01	ND	5.23	2.85	ND	7.25
dihydroxyacetone	0.98	0.53	ND	ND	0.33	ND	0.41	1.99
pyruvic acid	2.50	0.57	2.75	3.62	1.01	0.69	3.46	0.82
glycolic acid	0.23	ND	ND	7.12	ND	ND	7.04	0.14
lactic acid	4.35	7.01	ND	3.04	ND	0.51	2.84	0.91
formic acid	8.57	5.26	5.48	12.63	1.86	7.64	18.11	0.90
acetic acid	1.70	1.14	2.00	6.32	ND	1.25	7.83	0.64
levulinic acid	5.33	1.14	ND	ND	ND	5.05	ND	0.10

^a ND = not detected.

several factors are involved in the decomposition reactions. It seems that the main parameter in regard to the yield of HMF is the formation of polymers as a side reaction. Montgomery and Wiggins,⁴⁵ in their studies on the mechanism of dehydration of fructose under normal temperature and pressure conditions, noted that there was a competition reaction between the production of HMF and polymerization reactions. It seems also in the sub-CW condition that not only pH, but also the acid type has some influence on the stability of intermediates in the formation of HMF and/or soluble polymers. On the other hand, pH and acid types can control the rehydration reaction of HMF to levulinic and formic acids; therefore, the yield of HMF may be influenced by these side reactions.

The phosphoric acid was selected for further studies, because it has higher activity toward the formation of HMF. The other acids showed lower HMF yield than the use of phosphoric acid under identical conditions. Because the maleic, oxalic, and citric

acids slightly decomposed under sub-CW conditions, formic and acetic acids were identified from the decomposition reactions. HCl showed a greater catalytic effect on the rehydration of HMF to levulinic and formic acids (at lower pH values); therefore, the yield of HMF was lower, because of the decomposition of HMF.

3.3. Phosphoric Acid Catalyst: The Effect of Temperature and Residence Time. The decomposition products of fructose in the presence of a phosphoric acid catalyst at pH 2, as functions of temperature and residence time, are shown in Figures 4 and 5, respectively. Unreacted fructose was not identified after the reaction at temperatures of >523 K and/or residence times of >135 s; the HMF showed a maximum yield in the temperature range of 503–523 K (Figure 4a). The results of Figure 5a shows a maximum HMF yield at ~120 s. However, because the yield–temperature and yield–time curves showed no sharp peaks, small variations in the residence time and temperature cannot affect the reproducibility of the production

Table 2. (Continued)^a

products	HCl	H ₂ SO ₄	H ₃ PO ₄	citric acid	maleic acid	PTSA	oxalic acid	uncatalyzed
(d) pH 3								
HMF	33.37	28.52	30.86	4.73	28.90	15.50	5.00	18.08
furfural	2.20	1.70	1.47	0.45	3.13	1.68	0.52	2.14
fructose	25.23	35.28	4.85	ND	25.38	36.92	0.34	43.06
glucose	1.97	4.15	2.26	ND	2.28	1.34	0.15	2.70
glyceraldehyde	6.56	8.71	0.51	ND	4.24	5.87	1.22	3.78
glycolaldehyde	5.14	4.33	7.62	9.28	6.24	3.23	12.01	3.70
erythrose	1.45	1.20	2.25	3.51	2.19	1.00	4.35	2.11
formaldehyde	0.55	4.76	ND	ND	0.69	2.95	ND	5.70
pyruvaldehyde	8.30	9.45	1.21	ND	6.47	8.68	ND	7.25
dihydroxyacetone	2.64	6.00	ND	ND	1.42	1.17	0.25	1.99
pyruvic acid	2.71	0.76	3.66	3.83	1.33	0.67	3.75	0.82
glycolic acid	ND	ND	1.24	7.54	ND	ND	7.95	0.14
lactic acid	2.76	1.59	0.54	2.44	ND	0.29	2.30	0.91
formic acid	3.78	2.54	7.92	13.8	1.93	3.02	14.37	0.90
acetic acid	0.65	ND	4.82	8.28	ND	1.26	9.54	0.64
levulinic acid	ND	ND	ND	ND	ND	ND	ND	0.10
(e) pH 4								
HMF	17.25	14.89	13.51	1.47	8.11	2.15	1.20	18.08
furfural	0.87	0.66	0.95	0.30	1.46	1.15	0.42	2.14
fructose	37.29	46.92	4.77	ND	7.46	31.15	0.18	43.06
glucose	3.04	1.50	2.43	ND	2.81	1.93	0.09	2.70
glyceraldehyde	7.09	6.48	0.69	ND	1.26	6.25	0.50	3.78
glycolaldehyde	4.90	5.68	9.65	6.86	8.75	3.92	5.25	3.70
erythrose	1.23	1.50	2.85	2.01	3.30	1.62	2.01	2.11
formaldehyde	0.42	3.59	ND	ND	0.51	2.45	ND	5.70
pyruvaldehyde	22.41	10.68	1.21	ND	2.28	10.16	ND	7.25
dihydroxyacetone	5.39	1.14	ND	ND	1.37	1.53	0.12	1.99
pyruvic acid	0.83	1.36	4.17	3.88	2.45	0.92	3.45	0.82
glycolic acid	ND	0.53	2.35	9.40	3.49	ND	10.62	0.14
lactic acid	4.43	6.67	0.98	2.48	2.26	0.79	2.03	0.91
formic acid	4.09	4.33	11.76	12.53	4.44	4.93	11.51	0.90
acetic acid	1.21	1.90	7.90	10.81	5.00	2.44	13.51	0.64
levulinic acid	ND	ND	ND	ND	ND	ND	ND	0.10
(f) pH 5 ^b								
HMF		7.18	0.50	1.46	2.00	0.70	18.08	
furfural		0.99	ND	0.60	0.10	0.32	2.14	
fructose		4.45	ND	6.01	26.43	0.13	43.06	
glucose		2.32	ND	2.80	3.12	0.06	2.70	
glyceraldehyde		0.75	ND	0.50	6.00	0.27	3.78	
glycolaldehyde		9.86	3.46	9.64	4.51	4.14	3.70	
erythrose		2.97	0.90	3.60	2.46	1.20	2.11	
formaldehyde		ND	ND	0.06	0.62	2.41	5.70	
pyruvaldehyde		0.96	ND	0.56	7.96	ND	7.25	
dihydroxyacetone		ND	ND	1.45	2.95	ND	1.99	
pyruvic acid		4.04	3.13	3.58	1.18	3.05	0.82	
glycolic acid		2.90	11.12	4.65	0.70	11.42	0.14	
lactic acid		1.08	3.13	3.65	1.41	2.65	0.91	
formic acid		12.79	11.91	6.56	6.50	9.87	0.90	
acetic acid		9.31	14.32	5.67	3.55	14.97	0.64	
levulinic acid		ND	ND	ND	ND	ND	ND	0.10

^a ND = not detected. ^b No HCl or H₂SO₄ experiments were performed at pH 5.

yield of HMF. The concentrations of byproducts were negligible (see Figure 4b and c).

3.4. Effect of Initial Concentration of Fructose (with Phosphoric Acid Catalyst). For economic reasons, the initial fructose concentration should be as high as possible. Figure 6 shows the dependence of HMF yield on the initial concentration of reactant. The HMF yield decreased linearly as the initial concentration of fructose increased.

The yield of HMF in an initial fructose concentration of 1 M was ~3% lower than that in an initial fructose concentration of 0.06 M. The formation of solid humin was started at initial concentrations of >0.06 M and increased continuously with the concentration of fructose. In contrast, higher fructose concentrations lead to almost lower HMF yields.

It has been reported¹⁵ that, under normal temperature and pressure reaction conditions, in the case of a higher initial concentration of fructose, there is the possibility of polymerization and a destabilizing effect of fructose on HMF. It seems that, under the

sub-CW condition, for the same reason, the yield of HMF decreased by increasing the initial concentration of fructose. Generally, humin is a solid polymeric byproduct, the structure of which has not been elucidated yet. The amount of humin produced was calculated from its weight. Humin was detected by filtration and dried under vacuum, and an elemental analysis of humin exhibited a composition of 65.5% carbon and 4.4% hydrogen.

To obtain the high ratio of reactant to catalyst, a series of experiments was conducted with variation in the concentration of both the reactant and the catalyst. The high ratio (without decreasing the yield of HMF and producing humin) was ~2 (0.06 M initial fructose and 0.03 M phosphoric acid). Note that, to increase the ratio, it is possible to (a) increase the initial concentration of fructose, but as explained before, this produces solid humin at concentrations higher than 0.06 M, and (b) decrease the concentration of phosphoric acid; however, note that the minimum limit for the concentration to maintain a constant pH of 2 is 0.03 M.

Table 3. Comparison Series of HCl- and H₂SO₄-Catalyzed Experiments in the Absence and Presence of NaCl and Na₂SO₄, Conducted at pH 1.5, 513 K, a Residence Time of 120 s, and an Initial Fructose Concentration of 0.05 M, as a Function of the Absolute Yield of Reactant and Products^a

products	[a] 0.03 M HCl	[b] 0.015 M H ₂ SO ₄	[c] 0.03 M HCl + 0.05 M Na ₂ SO ₄	[d] 0.015 M H ₂ SO ₄ + 0.05 M NaCl	[e] 0.03 M HCl + 0.015 M H ₂ SO ₄ ^b
HMF	9.01	28.45	22.96	24.47	17.50
furfural	4.08	2.13	1.17	1.35	3.03
fructose	ND	0.22	6.61	ND	ND
glucose	ND	0.21	2.60	ND	0.16
glyceraldehyde	ND	0.48	2.47	ND	0.66
glycolaldehyde	ND	2.33	6.85	2.54	3.64
formaldehyde	ND	0.70	1.76	ND	0.70
dihydroxyacetone	ND	1.30	1.43	ND	1.39
pyruvic acid	1.15	0.66	5.66	1.09	0.89
glycolic acid	ND	ND	1.42	ND	ND
lactic acid	5.05	9.39	6.15	8.01	12.05
formic acid	50.68	23.12	9.15	32.92	33.96
acetic acid	1.10	1.08	5.61	1.07	0.93
levulinic acid	46.08	17.50	0.70	28.21	30.22

^a ND = not detected. ^b 1:1 mixture (v/v).

Table 4. Absolute Yield of HMF and Other Byproducts Obtained upon Decomposition of Saccharides (0.05 M) at 513 K and a Residence Time of 120 s, in the Presence of Phosphoric Acid (0.1 M, pH 2)^a

products	Reactants						
	D-fructose	L-sorbose	D-mannose	D+-(−)galactose	D-glucose	sucrose ^b	cellobiose ^b
HMF	65.30	50.03	31.11	27.30	30.03	40.17	27.25
furfural	3.90	1.14	1.01	1.16	1.21	2.15	1.80
fructose	ND	ND	ND	ND	3.62	3.78	4.09
glucose	0.39	ND	ND	ND	ND	18.87	55.93
glycolaldehyde	1.47	0.99	ND	ND	ND	ND	ND
formaldehyde	ND	ND	ND	3.48	4.38	3.48	4.44
pyruvic acid	1.99	5.56	ND	ND	ND	0.14	ND
formic acid	3.73	3.71	1.34	1.20	ND	1.95	ND
acetic acid	1.52	1.73	ND	ND	ND	ND	ND
1,6-anhydroglucose	ND	ND	ND	ND	4.27	2.32	3.63
unreacted	2.08	0.67	57.88	48.01	52.38	ND	0.62

^a ND = not detected. ^b Calculations are based on C6.

Table 5. Comparison Series of Iron Contents of Batch Reactors after Sub-CW Treatment in Presence of Different Acids at pH 2, Sub-CW Temperature of 513 K for 120 s

acid type	iron content (mg Fe ions/one reactor (120 g))
HCl	3.60
H ₂ SO ₄	0.50
H ₃ PO ₄	0.50
citric acid	0.46
maleic acid	0.41
PTSA	0.52
oxalic acid	0.34
uncatalyzed	none detected

3.5. Acid Catalyst Decomposition of Other Saccharides.

Generally, it is possible that other C-6 carbon sugars (i.e., aldohexoses and ketohexoses) catalytically dehydrate to HMF. Under the optimum sub-CW conditions (513 K and a residence time of 120 s) in the presence of phosphoric acid as a catalyst at pH 2, the decomposition reactions of various monosaccharides and two disaccharides were studied. The results are shown in Table 4.

3.5.1. Decomposition of Aldohexoses. The sub-CW decomposition of glucose, which is main C-6 sugar, showed HMF at lower yield than fructose. A generally lower reactivity of glucose (and other aldoses, such as galactose and mannose), as compared with fructose (and other ketoses such as sorbose), was largely explained by the much lower relative abundance of acyclic glucose, as compared to that of acyclic fructose in normal temperature and pressure.⁴⁸ It seems that, under sub-CW conditions, a shortage of the acyclic form of glucose also causes a lower yield of HMF. The isomerization results of glucose and fructose to each other (from Table 4) shows the possibility of

the isomerization of aldohexoses to ketohexoses and vice versa under sub-CW conditions. The decomposition behaviors of mannose and galactose were similar to glucose. There was no big difference between amounts of un-reacted reactants and HMF yield. However in glucose and galactose, ~3%–4% of formaldehyde, which was not identified in mannose was detected. On the other hand decomposition of mannose and galactose showed small amount of formic acid.

3.5.2. Decomposition of Ketohexoses. In the comparison of two ketohexoses (i.e., fructose and sorbose), more interestingly, the yield of HMF from sorbose was observed to be smaller than that of fructose (see Table 4). Ishida et al.⁴⁹ have studied the

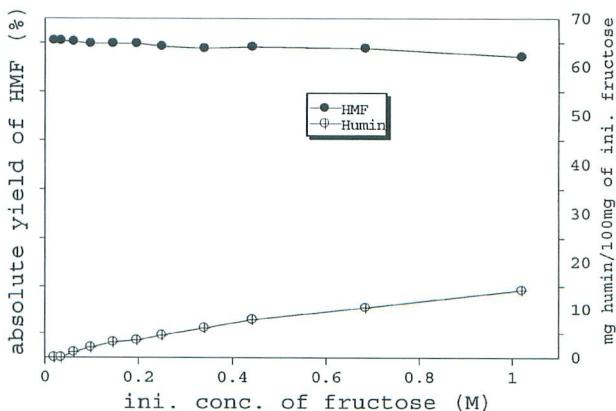


Figure 6. Dependence of product yields as a function of the initial concentration of fructose at 513 K and a residence time of 120 s in the presence of phosphoric acid (0.1 M, pH 2).

comparison reactions of ketohexoses (i.e., fructose and sorbose, which possesses different C-3 and C-4 hydroxyl configurations) in a normal system. They determined that the hydroxyl groups at the 1 and 3 positions of fructose were suggested to be involved in the dehydration reaction. It seems that, in sub-CW, the same reason causes the higher yield of HMF from fructose than sorbose. However, the amount of other byproducts was almost similar in both fructose and sorbose.

3.5.3. Decomposition of Disaccharides. The facile and rapid hydrolysis of sucrose in sub-CW results in the formation of glucose and fructose. Haworth and Jones²¹ have shown that, when sucrose was heated in water at 418 K, in the presence of oxalic acid as a catalyst, most of the fructose was reacted, while the glucose component remained essentially unchanged. However, our experimental results, in sub-CW, showed that not only the hydrolysis of sucrose to fructose and glucose occurred, but also a sequence of dehydration reaction of both of them in the formation of HMF occurred. Approximately 18.9% and 3.8% of glucose and fructose were determined to be unchanged, which showed less reactivity of glucose, compared to fructose.

Cellobiose, which was used as a model material for cellulose in this study, can be decomposed via hydrolysis of the glycosidic bond to produce glucose (see Table 4). The sub-CW treatment of cellobiose shows >99% decomposition to glucose under optimum conditions. The glucose that is formed undergoes further decomposition to HMF and other byproducts. A small amount of 1,6-anhydroglucoside, which is a byproduct of the dehydration of glucose and glucose containing saccharides, was also detected.

3.6. Effect of Acids on the Corrosion of Sub-CW Reactors. Table 5 shows the comparison series of the corrosion of sub-CW reactors after sub-CW reaction at a temperature of 513 K for 120 s, as function of different types of acid at initial pH of 2. The result of the uncatalyzed reaction is also shown. In the presence of inorganic and organic acids, Fe ions were identified, the amount of which was in direct relation with the amount of corrosion of the reactors. The results showed that, in the presence of acids, the corrosion amounts increased; particularly, with HCl, compared to other acids, greater corrosion was observed. However, the corrosion in the case of phosphoric acid is almost the same as that of other acids (except for HCl). It was found that, by increasing the residence time, or reaction temperature, and, conversely, by decreasing the initial pH of solution, the corrosion amount increased.

4. Conclusion

The application of subcritical water (sub-CW), which is a simple, clean, and environmentally friendly method, for the dehydration of fructose has been determined to be a feasible process. Although, under the normal temperature and pressure conditions, the presence of acid catalysts is necessary for the production of 5-hydroxymethyl furfural (HMF), the dehydration of fructose to HMF can be conducted even in the absence of acid catalysts. However, in the presence of acids, the amount of conversion of fructose to HMF increased.

On the other hand, the pH of the solution, the nature of the acid, the initial fructose concentration, the sub-CW temperature, and the residence time each influenced the production yield of HMF and byproducts. The investigation of the effect of acid type and its pH on the conversion of fructose to HMF was an essential aim of this study. We found that phosphoric acid showed good catalytic ability on the dehydration of fructose in sub-CW. That is, an ~65% absolute yield of HMF was obtained using a phosphoric acid catalyst.

At low concentrations of fructose, polymers as byproducts remained dissolved; therefore, this reaction can be conducted in continuous tubular subcritical reactors without the problem of plugging. We believe that further improvements in the yield of this valuable product require conditions that reduce the parameters, mainly those which have influence on the polymerization reactions. From a catalytic view of point, modification of this reaction could include the use of heterogeneous acids instead of homogeneous acids under sub-CW conditions, which is under investigation.

This method is also able to convert other saccharides to HMF. In the present study, we selected fructose as a model of the hexose sugars. The conversion of waste materials that contain aldoses such as woody biomasses to HMF is possible in sub-CW.

Although the yield of HMF from glucose-containing carbohydrates as the main C-6 sugars is lower, the recent introduction of a commercial process for isomerizing glucose to fructose²³ may add the possibility of converting glucose waste to more-reactive fructose for subsequent reaction, using the sub-CW system to increase production yields.

Finally, the decomposition of fructose is a consecutive-type reaction, in which the HMF produced can be rehydrated to levulinic and formic acids. HCl exhibited good catalytic activity in the rehydration reaction, compared to other acid catalysts used in this report. The effect of HCl as a catalyst in the formation and decomposition of HMF to levulinic and formic acids is under investigation.

Acknowledgment

The financial support from The Ministry of Education, Culture, Sports, Science and Technology of Japan in the form of 21st Century COE program (E19, Science and Engineering for Water Assisted Evolution of Valuable Resources and Energy from Organic Wastes) for part of this research is gratefully acknowledged.

Literature Cited

- Dinaro, J. L.; Howard, J. B.; Green, W. H.; Tester, J. W.; Bozzelli, J. W. Analysis of an elementary reaction mechanism for benzene oxidation in supercritical water. *Proc. Combust. Inst.* **2000**, *28*, 1529.
- Kubatova, A.; Miller, D. J.; Hawathorne, S. B. Comparison of subcritical water and organic solvents for extracting Kava lactones from Kava root. *J. Chromatogr., A* **2001**, *923* (1–2), 187.
- Yoshida, H.; Nakahashi, T. Production of useful substances from meat and bone meal by subcritical water hydrolysis. In *Proceedings of the 10th Asian Pacific Confederation of Chemical Engineering (APCChE)*, Kitakyushu, Japan, October 2004, A-272.
- Yoshida, H.; Tavakoli, O.; Hirata, Y. Conversion of scallop viscera wastes to valuable compounds using sub-critical water. In *Proceedings of the 10th Asian Pacific Confederation of Chemical Engineering (APCChE)*, Kitakyushu, Japan, October 2004, A-273.
- Yoshida, H.; Terashima, M.; Takahashi, Y. Production of organic acids and amino acids from fish meat by sub-critical water hydrolysis. *Biotechnol. Prog.* **1999**, *15*, 1090.
- Yoshida, H.; Tavakoli, O. Sub-critical water hydrolysis treatment for waste squid entrails and production of amino acids, organic acids, and fatty acids. *J. Chem. Eng. Jpn.* **2004**, *37* (2), 253.
- Oomori, T.; Khajavi, S. H.; Kimura, Y.; Adachi, S.; Matsuno, R. Hydrolysis of disaccharides containing glucose residue in subcritical water. *Biochem. Eng. J.* **2004**, *18*, 143.
- Minowa, T.; Inoue, S. Hydrogen production from biomass by catalytic gasification in hot compressed water. *Renewable Energy* **1999**, *16*, 1114.
- Moreschi, S. R. M.; Petrante, A. J.; Meireles, M. A. A. Hydrolysis of ginger bagasse starch in subcritical water and carbon dioxide. *J. Agric. Food Chem.* **2004**, *52*, 1753.
- Fleche, G.; Gaset, A. Process for manufacturing 5-hydroxymethylfurfural. U.S. Patent No. 4,339,387, July 13, 1982.

- (11) Antal, M. J.; Mok, W. S. A study of the acid-catalyzed dehydration of fructose in near-critical water. *Res. Thermochem. Biomass Convers.* **1988**, 464.
- (12) Antal, M. J., Jr.; Mok, W. S. L.; Richards, G. N. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose. *Carbohydr. Res.* **1990**, 199, 91.
- (13) Bicker, M.; Hirth, J.; Vogel, H. Dehydration of fructose to 5-hydroxymethylfurfural in sub- and supercritical acetone. *Green Chem.* **2003**, 5, 280.
- (14) Lewkowski, J. Synthesis, chemistry and applications of 5-hydroxymethylfurfural and its derivatives. *Arkivoc* **2001**, 2 (6), 17.
- (15) Lansalot-Matras, C.; Moreau, C. Dehydration of fructose into 5-hydroxymethylfurfural in the presence of ionic liquids. *Catal. Commun.* **2003**, 4, 517.
- (16) Kuster, B. F. M.; van der Baan, H. S. The influence of the initial and catalyst concentrations on the dehydration of D-fructose. *Carbohydr. Res.* **1977**, 54, 165.
- (17) Harris, D. W.; Feather, M. S. Intermolecular C-2 → C-1 hydrogen transfer reactions during the conversion of aldoses to 2-furaldehydes. *J. Org. Chem.* **1974**, 39 (5), 724.
- (18) Moye, C. F.; Goldsack, R. J. Reaction of ketohexoses with acid in certain nonaqueous sugar solvents. *J. Appl. Chem.* **1966**, 16, 206.
- (19) Szmant, H. H.; Chundury, D. D. The preparation of 5-hydroxymethylfurfuraldehyde from high fructose corn syrup and other carbohydrates. *J. Chem. Technol. Biotechnol.* **1981**, 31, 135.
- (20) Mendnick, M. L. Acid-catalyzed conversion of aldohexose into 5-(hydroxymethyl)-2-furfural. *J. Org. Chem.* **1962**, 27, 398.
- (21) Haworth, W. N.; Jones, W. G. M. Conversion of sucrose into furan compounds. I. 5-hydroxymethylfurfuraldehyde and some derivatives. *J. Chem. Soc.* **1944**, 667.
- (22) Chen, J.-D.; Kuster, B. F. M.; Wiele, D. K. V. Preparation of 5-hydroxymethylfurfural via fructose acetonides in ethylene glycol dimethyl ether. *Biomass Bioenergy* **1991**, 1 (4), 217.
- (23) Jow, J.; Rorrer, G. L.; Hawley, M. C. Dehydration of D-fructose to levulinic acid over LZY zeolite catalyst. *Biomass* **1987**, 14, 185.
- (24) Moreau, C.; Durand, R.; Pourcheron, C.; Razigade, S. Preparation of 5-hydroxymethylfurfural from fructose and precursors over H-form zeolites. *Ind. Crops Prod.* **1994**, 3, 85.
- (25) Lecomte, J.; Finiels, A.; Moreau, C. A new selective route to 5-hydroxymethylfurfural from furfural and furfural derivatives over microporous solid acidic catalysts. *Ind. Crops Prod.* **1999**, 19, 235.
- (26) Trapmann, H.; Sethi, V. S. Effect of Th and Zr ions on aldoses. *Arch. Pharm. (Weinheim, Ger.)* **1966**, 299, 9 (8), 657.
- (27) Jocs, R. E.; Lange, H. B. Conversion of invert maltooses. U.S. Patent No. 3,066,150, 1962.
- (28) Seri, K.-I.; Sakaki, T.; Shibata, M.; Inoue, Y.; Ishida, H. Lanthanum(III)-catalyzed degradation of cellulose at 250 °C. *Bioresour. Technol.* **2002**, 81, 257.
- (29) Schraufnagel, R. A.; Rasc, H. F. Levulinic acid from sucrose using acidic ion-exchange resins. *Ind. Eng. Chem. Prod. Res. Dev.* **1975**, 14 (1), 40.
- (30) Brown, D. W.; Floyd, A. J.; Kinsmann, R. G.; Roshan-Ali, Y. Dehydration reactions of fructose in nonaqueous media. *J. Chem. Technol. Biotechnol.* **1982**, 32, 920.
- (31) Neyret, C.; Louis, C.; Henri, N.; Gerard, D. Preparation of 5-hydroxymethylfurfural from saccharides. *Chem. Abstr.* CA117: 90121.
- (32) Garder, J. D.; Jones, R. F. Method for producing 5-hydroxymethylfurfural. U.S. Patent No. 3,483,228, 1969.
- (33) Stone, J. E.; Blundell, M. J. A micromethod for determination of sugars. *Can. J. Res.* **1950**, 28, 676.
- (34) Peniston, Q. P. Manufacture of 5-hydroxymethyl 2-furfural. U.S. Patent No. 2,750,394, 1956.
- (35) Nakamura, Y. Preparation of 5-(hydroxymethyl)furfural by selective dehydration of D-fructose. *Noguchi Kenkyusho Jiho* **1980**, 23, 25.
- (36) Rice, F. A. H. Effect of aqueous sulfuric acid on reducing sugars. *J. Org. Chem.* **1958**, 23, 465.
- (37) Jennings, J. M.; Bryon, T. A.; Gibson, J. M. Catalytic reduction in subcritical water. *Green Chem.* **2000**, 87.
- (38) Holgate, R. H.; Meyer, J. C.; Tester, J. W. Glucose hydrolysis and oxidation in supercritical water. *AIChE J.* **1995**, 41 (3), 637.
- (39) Kabymela, B. M.; Adschari, T.; Malaluan, R.; Arai, K. Rapid and selective conversion of glucose to erythrose in supercritical water. *Ind. Eng. Chem. Res.* **1997**, 36, 5063.
- (40) Kabymela, B. M.; Adschari, T.; Malaluan, R.; Arai, K. Degradation kinetics of dihydroxyacetone and glyceraldehyde in subcritical and supercritical water. *Ind. Eng. Chem. Res.* **1997**, 36, 2025.
- (41) Antal, M. J., Jr.; Mok, W. S. L.; Richards, G. N. Four-carbon model compounds for the reactions of sugars in water at high temperature. *Carbohydr. Res.* **1990**, 199, 111.
- (42) Benvenuti, F.; Carlini, C. Heterogeneous zirconium and titanium catalysts for the selective synthesis of 5-hydroxymethyl-2-furfuraldehyde from carbohydrates. *Appl. Catal., A* **2000**, 193, 147.
- (43) Kuster, B. F. M.; Temmink, H. M. G. The influence of pH and weak-acid anions on the dehydration of D-fructose. *Carbohydr. Res.* **1977**, 54, 185.
- (44) Kuster, B. F. M.; Tebbens, L. M. Analytical Procedures for Studying the Dehydration of D-Fructose. *Carbohydr. Res.* **1977**, 54, 159.
- (45) Montgomery, R.; Wiggins, L. F. Effect of heat on aqueous solutions of sucrose and other carbohydrates. *J. Soc. Chem. Ind.* **1947**, 66, 31.
- (46) Lourvani, K.; Rorrer, G. L. Reaction rates for partial dehydration of glucose to organic acids in solid-acid, molecular-sieving catalyst powders. *J. Chem. Technol. Biotechnol.* **1997**, 69 (1), 35.
- (47) Tyrlík, S. K.; Szerszen, D.; Olejík, M.; Danikiewicz, W. Selective dehydration of glucose to hydroxymethylfurfural and a one-pot synthesis of a 4-acetylbutyrolactone from glucose and trioxane in the solution of aluminum salts. *Carbohydr. Res.* **1999**, 315, 268.
- (48) Van Dam, H. E.; Kieboon, A. P. G.; Van Bekkum, H. The conversion of fructose and glucose in acidic media: formation of hydroxymethylfurfural. *Starch* **1986**, 38, 95.
- (49) Seri, K.-I.; Inoue, Y.; Ishida, H. Highly Efficient Catalytic Activity of Lanthanide(III) Ions for Conversion of Saccharides to 5-Hydroxymethyl-2-furfural in Organic Solvents. *Chem. Lett.* **2000**, 22.

Received for review September 29, 2005
Revised manuscript received January 30, 2006
Accepted January 31, 2006

IE051088Y