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# Kinetics of the Decomposition of Fructose Catalyzed by Hydrochloric Acid in Subcritical Water: Formation of 5-Hydroxymethylfurfural, Levulinic, and Formic Acids

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This paper deals with the dehydration of fructose (F) to 5-hydroxymethylfurfural (HMF) and the rehydration of HMF to levulinic acid (LA) along with formic acid (FA) in subcritical water (sub-CW) in the presence of HCl as catalyst. The experimental conditions were 483–543 K, 4–15 MPa, and residence times of 0.5–300 s. The pressure (in the range of 4–15 MPa) did not affect the decomposition reactions. This differed from other operating variables. The main products were found to be HMF, 2-furaldehyde (2FA), LA, FA, and soluble polymers. The HMF, LA, and FA were also individually subjected for decomposition at the same condition. We found that, during the sub-CW reaction, byproducts (soluble polymers) were produced not only from F but also from HMF. However, we distinguished between two different polymers (i.e., produced from the decomposition of F or HMF) in a proposed reaction model. The kinetics of the sub-CW reaction was developed by considering not only F, HMF, LA, and FA but also soluble polymers. The kinetic constants obtained from the proposed reaction pathway showed good agreement with experimental results.

## 1. Introduction

Sub- and/or supercritical water have been increasingly used for synthesis of various compounds and/or decomposition waste materials. The physical properties of water changes widely through pressure and temperature changes.<sup>1</sup> Sub- and supercritical water processing offer an alternative to older conventional chemical reactions, particularly reactions conducted in organic solvents that may be environmentally unacceptable.<sup>2</sup>

Recently, the growing interest in the conversion of biomass, carbohydrates, and other organic materials for production of useful chemical compounds has led to extensive research activity using subcritical water (sub-CW).<sup>3–8</sup> Many biobased building block chemicals can be produced from renewable resources via not only conventional but also sub-CW techniques. 5-Hydroxymethylfurfural (HMF) and levulinic acid (LA) are the examples that have been investigated in detail.

There has been interest in HMF since the last decade of the 19th century.<sup>9</sup> Because of its varied functionality, it can be utilized to produce a wide range of chemical intermediates or end-products.<sup>9,10</sup> Water at its critical status has properties that are different from water under normal conditions. For example, the relative dielectric constants of sub-CW at 473 and 573 K are comparable with those of methanol and acetone under ambient conditions, respectively. From another point of view, in the conventional methods, the yield of HMF cannot be increased because of oligomerization and polymerization reactions. However, a relatively higher yield of HMF in water under its critical point has already been reported.<sup>11</sup>

LA has been known since 1840 to result from the decomposition reaction of carbohydrates with mineral acids.<sup>12</sup> It is one of United States Department of Energy's (DOE's) top 12 bio-derived feedstocks,<sup>13</sup> because it can be used as a raw material for resins, plasticizers, textiles, animal feeds, coatings, antifreeze, and the like.<sup>14</sup>

The formation pathway of HMF and LA from the decomposition of saccharides is shown in Scheme 1. This reaction has been studied by a number of authors in conventional methods and recently in sub-CW.<sup>3,11,12,14–18</sup> Kuster and co-workers<sup>19</sup> studied the decomposition of F and the formation of HMF and LA in the presence of HCl. They derived differential equations based on their proposed model in order to calculate the kinetic constants of F, HMF, and LA. The decomposition pathways have also been studied using a sulfuric acid catalyst.<sup>15,20</sup>

In sub-CW, several studies on decomposition kinetics of different saccharides have also been examined. Adachi and co-workers<sup>21,22</sup> considered the kinetics of decomposition of monosaccharides (aldohexoses and ketohexose) and a disaccharide (sucrose) in sub-CW. Arai and co-workers<sup>23</sup> investigated the decomposition mechanism and kinetics of cellobiose in sub- and supercritical waters in a short residence time (0.04–2 s); and in another report, the kinetics of glucose decomposition under the same experimental conditions was studied.<sup>24</sup> In sub- and supercritical water systems, the kinetics of cellobiose decomposition was studied at very short residence times,<sup>25</sup> and the desired product was glucose; however, HMF as a byproduct was identified and investigated. Decomposition kinetics of maltose in sub-CW was investigated at longer residence times up to 600 s,<sup>26</sup> and glucose and HMF were identified as decomposition products; however, this study was mainly concerned with the decomposition kinetics of substrate.

There are no available reports on the kinetic study of the decomposition of F and the formation of HMF, LA, and FA, including their decomposition products as well as soluble polymers under sub-CW conditions. The objective of this work is to propose a model for the decomposition of F (HMF, LA, and FA) and the formation of products in (continuous) sub-CW condition in the presence of HCl acid catalyst, and from the proposed model, by matching experimental and calculated data, we obtained the rate constants.

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Scheme 1. General Decomposition Pathway of F

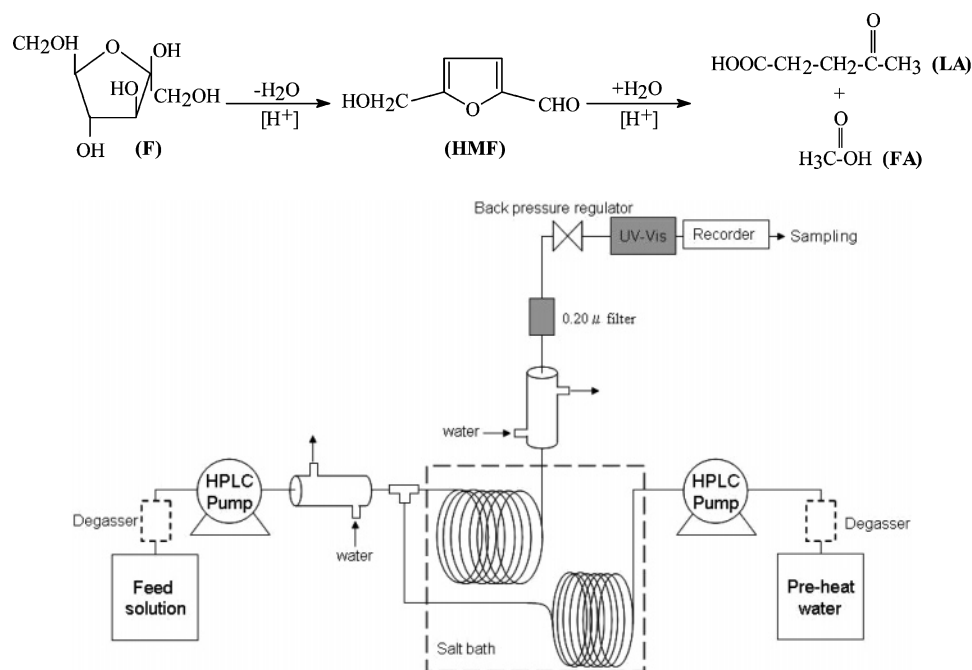


Figure 1. Experimental setup for flow-type sub-CW.

## 2. Experimental Section

**2.1. Materials.** Chemicals (analytical grade) used in the experiments, calibration curves, and high-performance liquid chromatography (HPLC) mobile phases were the following: F (fructose), glucose, HMF (5-hydroxymethylfurfural), 2FA (2-furaldehyde), LA (levulinic acid), FA (formic acid), pyruvic acid, malic acid, lactic acid, acetic acid, *p*-toluenesulfonic acid, and methanol; all were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

**2.2. Apparatus.** We used home-built continuous sub-CW equipment depicted schematically in Figure 1. The tube of this equipment, made of stainless steel 316 with i.d. 0.25 mm (Swagelok AG, Switzerland), allowed a wide range of residence times required to study the decomposition reaction of substrates and the formation of products. The feed solution and the preheat water initially passed through the multichannel degasser (Shimadzu degasser DGU-14A, Shimadzu Co., Japan). Two HPLC pumps (Shimadzu, LC-10AT, Shimadzu Co., Japan) were used to pump the feed solution and the preheat water to the reactor at the required flow rates, respectively, which depended on the required residence times in the reactor. The preheat water after heating up to the same temperature as the reaction temperature was mixed with the feed solution and then passed through the reactor inside the salt bath. Flow rates of the feed solution and the preheat water have been adjusted in order to stay in the laminar flow regime and have a minimum deviation from an ideal isothermal plug-flow reactor. Two single-path heat exchangers were used to cool the solutions to  $0 \pm 1$  °C before and after reaction. A back-pressure regulator (Tescom Corporation, Japan) was used to maintain the pressure at the desired values.

At the end of the line of equipment, a UV-vis detector (Shimadzu SPD-10AVP, Shimadzu Co., Japan) with a recorder (Shimadzu C-R5A Chromatopac, Shimadzu Co., Japan) was positioned to monitor the total absorbance of the outlet reaction solution. Figure 2 shows a typical absorbance of the outlet solution as a function of time. This curve indicates the time needed for steady-state conditions after changing the experi-

mental condition such as temperature, pressure, and/or flow rate. It is obvious that, by changing any experimental conditions, the steady-state condition can be defined as a time needed to obtain constant absorbance of the total products.

**2.3. Procedure.** The initial concentrations of F and other substrates (i.e., HMF, LA, and FA) were kept low at 0.5% in order to avoid problems with the formation of solid materials. The pH of the feed solution was adjusted to 1.5 using HCl as the acid catalyst. For the preheat water, the milli-Q water (neutral pH) was used.

The pH of the feed solution after mixing with preheat water was found to be from 1.5 to 1.8, before the reaction started. The residence time ( $\tau$ ) was calculated by eq 1,

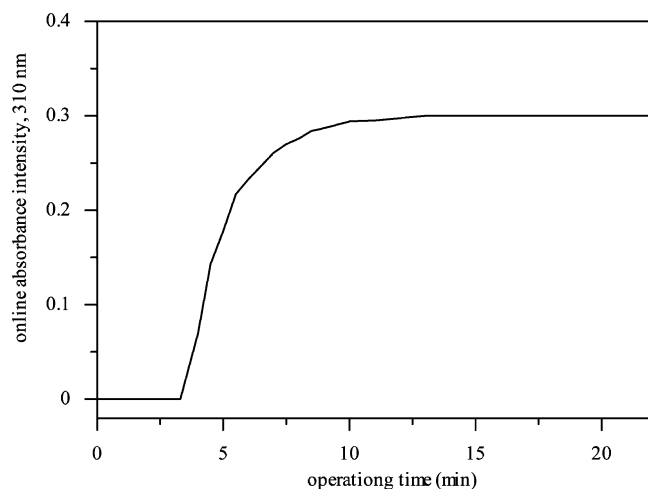
$$\tau = V\rho F_r^{-1} \quad (1)$$

where  $V$  is the reactor volume,  $F_r$  is the mass flow rate, and  $\rho$  is the density (at sub-CW conditions) of the reaction mixture. The density was assumed to be that of pure water because very dilute samples were used. The densities of water under sub-CW conditions were calculated from the literature.<sup>27</sup>

The reaction temperature was fixed at 483, 513, and 543 K using pressures of 4, 8, and 15 MPa and residence times between 0 and 300 s. Samples were taken at different residence times between 0 and 300 s and analyzed for remaining substrate and decomposition products.

**2.4. Analysis.** A CSPAK narrow-bore column C18 (2.1 × 100 mm) from Chromato Science. Co. Ltd. (Japan) in a HPLC using two Varian ProStar210 (Varian Inc., U.S.A.) solvent-delivery modules coupled with electrospray ionization mass spectrometry (ESI-Varian 1200 Quadrupole MS/MS, Varian Inc., U.S.A.) and/or PDA (photodiode array) detector (Varian PDA 330 Detector, Varian Inc., U.S.A.) was used for identification and quantitative analysis of products. For the detection of the HMF and the furfural, the PDA wavelength was set to 284 nm. The HPLC column was held at ambient temperature.

Concentrations of organic acids (levulinic, formic, pyruvic, malic, lactic, and acidic acids) were determined by a HPLC



**Figure 2.** Time needed for steady-state condition to be established in a typical flow-type sub-CW at 513 K and 4 MPa.

using a Shimadzu LC-10AD VP (Shimadzu Co., Japan) pump with two ion-exclusion chromatography columns (Shim-pack SCR-102H, 8 × 300 mm, Shimadzu Co., Japan) in series, and their detection was affected by using postcolumn pH-buffered electroconductivity detection (Shimadzu CDD-6A, Shimadzu Co., Japan). The mobile phase consisted of 5 mM of *p*-toluenesulfonic acid (hereafter called PTSA) solution at a flow rate of 0.8 mL/min. Mixtures of 5 mM of PTSA and 100 mM of ethylenediaminetetraacetic acid (EDTA) were used as post-column reagents, both at flow rates of 0.8 mL/min. The column temperature was kept at 313 K.

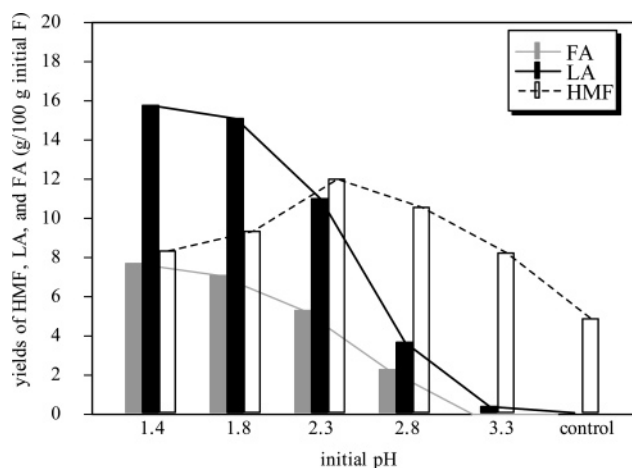
Two size-exclusion chromatography columns in series (Shodex-Sugar KS 804 and KS801, 8 × 300 mm, Shodex Co., Japan) in a HPLC in conjunction with a Jasco PU-2080 plus (Jasco Corp., Japan) pump coupled to a refractive index detector (Jasco, RI 2031 plus, Jasco Corp., Japan) were used for quantitative analysis of products that could not be detected using a UV detector. This HPLC system was operated at an oven temperature of 303 K using water at 0.4 mL/min flow rate as a mobile phase.

The pH of all solutions was measured using a glass pH-electrode attached to a Horiba pH/ion meter f-23 (Horiba Co, Japan). A double beam UV–visible spectrophotometer Shimadzu UV-160A (Shimadzu Co., Japan) was used for all spectrophotometric measurements. Elemental analysis was performed using inductively coupled plasma–atomic emission spectrophotometry (ICP–AES) (SPS-7800 plasma spectrometer, Seiko, Japan). The Fe ions of the aqueous phase after the sub-CW reaction without dilution were directly determined using ICP equipment.

### 3. Results and Discussion

**3.1. Effect of Initial pH of Feed Solution on Decomposition of F in sub-CW.** Our previous studies using batch-type sub-CW reactors have shown<sup>11</sup> that, in the presence of HCl, HMF was produced from the dehydration of F, which consequently undergoes rehydration to LA and FA (see Scheme 1). The yields of HMF, LA, and FA were found to be dependent on the initial pH of the solution.

In this work, in order to see the effect of the initial pH of the F solution on the reaction products, the pH of the feed solution (F) was adjusted to 1.0, 1.5, 2.0, 2.5, and 3.0, respectively. The pH of the solution after mixing with preheat water (1:1, before entering to the reactor) increased to 1.4, 1.8, 2.3, 2.8, and 3.3,



**Figure 3.** Yields of HMF, LA, and FA as a function of pH of initial solution adjusted with HCl in flow-type sub-CW at 513 K, 4 MPa, and 100 s residence time.

**Table 1.** Identified Products from Typical Decomposition of F and Other Substrates in Presence of HCl at pH 1.8 in sub-CW at a Temperature of 513 K and a Residence Time of 100 s

substrate				
	F	HMF	LA and/or FA <sup>a</sup>	
a	HMF	a'	-	a''
b	2FA	b'	-	b''
c	LA	c'	LA	c''
d	FA	d'	FA	d''
e	soluble polymers <sup>b</sup>	e'	soluble polymers	e''
f	pyruvic acid <sup>c</sup>	f'	-	f''
g	malic acid <sup>c</sup>	g'	-	g''
h	lactic acid <sup>c</sup>	h'	lactic acid <sup>3</sup>	h''
i	acetic acid <sup>c</sup>	i'	acetic acid <sup>3</sup>	i''

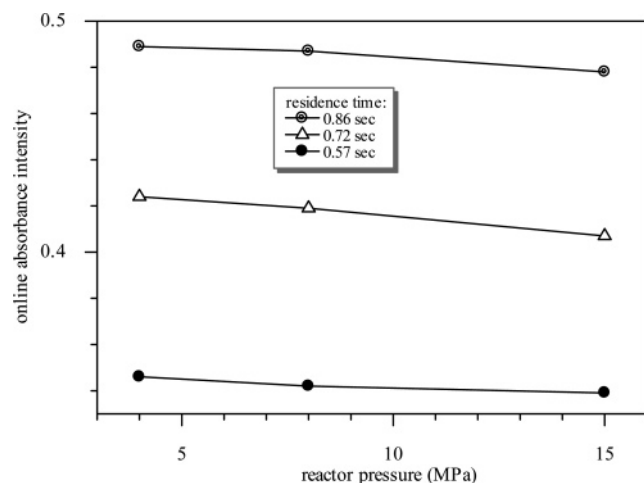
<sup>a</sup> Did not identify any decomposition compounds. <sup>b</sup> Absorbance at 350–450 nm corresponding to these polymers. <sup>c</sup> Minor products.

respectively. Figure 3 shows the HMF, LA, and FA yields as a function of pH at 513 K and 100 s residence time in the flow reaction. More than 99% of the F decomposed at the experimental condition. By decreasing the pH, the yield of HMF, and consequently the yields of LA and FA (from the rehydration of HMF), increased. HMF showed a maximum yield at pH 2.3, which decreased by decreasing pH. The highest yields of LA and FA were obtained at pH 1.4. In conclusion, more acidic conditions were necessary to achieve higher yields of LA and FA from F.

For the formation of LA and FA from F, the HMF is initially produced and then rehydrated to LA and FA. Therefore, we selected the initial pH between 2.3 and 1.4 (that is, pH 1.8) for the study of the decomposition of F, the formation of HMF, and its rehydration products. It is worth noticing that, at pH 1.4, higher total yields of HMF, LA, and FA can be relatively obtained. However, in order to avoid more corrosion of reaction pipes, the initial pH of 1.8 was selected for further studies.

**3.2. Decomposition Products.** All of the reaction products are listed in Table 1. Some other minor decomposition products were also identified. No decomposition products were identified from LA and FA.

Soluble polymers could not be quantitated. The isomerization of F to glucose has been reported using batch type sub-CW at short residence times.<sup>11,29</sup> Moreover, we did not identify glucose production at any residence time; there is the possibility of quick decomposition producing glucose to other products such as soluble polymers and HMF.



**Figure 4.** Typical three online absorbance intensities at 310 nm of outlet solution of flow-type sub-CW decomposition of F as a function of reactor pressure at 513 K and initial pH 1.8 using HCl.

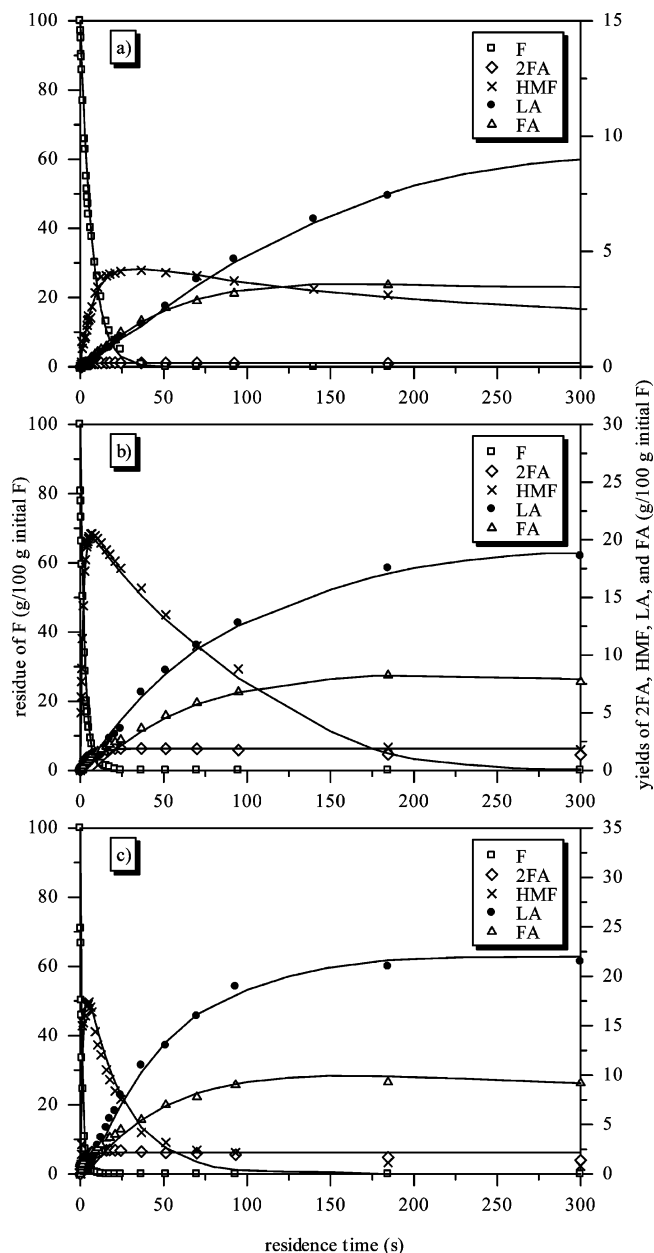
**3.3. Effect of Pressure on Decomposition of F.** The effect of pressure on the decomposition reactions of F was investigated at a constant reaction temperature of 513 K. Three different pressures, 4, 8, and 15 MPa, were selected. Generally, the effect of pressure on most properties of water such as density and dielectric constant in sub-CW conditions is small.<sup>24</sup> Pressure has a much weaker influence on the dielectric constant of water than temperature, which increases only slightly with increasing pressure.<sup>30</sup>

Figure 4 shows the absorbance intensity of the outlet solution from the flow-type sub-CW system as a function of pressure. The effect of pressure on the absorbance of the reaction products was small, and it is possible that the total experimental error overlaps the physical effects accompanying the pressure variation. Because the reaction is independent of pressure, a lower reactor pressure of 4 MPa was selected for further studies.

**3.4. Decomposition Profiles of F, HMF, LA, and FA.** A series of decomposition experiments of F were conducted under various temperatures at 4 MPa, and decomposition profiles were obtained accordingly up to 300 s. To obtain more insight into reaction paths, the HMF, LA, and FA were treated under the same conditions. Figures 5, 6, 7, and 8 show the profiles of F, HMF, LA, and FA at 483, 513, and 543 K with an initial pH of 1.8 and 0.5% concentration of each substrate as a function of residence time, respectively. The solid lines are the theoretical lines calculated from the model proposed.

**3.4.1. Decomposition of Fructose.** As shown in Figure 5, the time for conversion of 99% of F decreased from 40 to 10 s by increasing the reaction temperature from 483 to 543 K. The HMF produced from the dehydration of F peaked between 5 and 25 s (depending on the reaction temperature). By extending the reaction time, HMF underwent further rehydration to LA and FA; their amounts increased with time within 200 s. In addition, as will be shown later, there is a possibility of decomposition of LA and FA in longer sub-CW conditions; therefore, at longer residence times, the yields of both LA and FA decrease somewhat, particularly at the higher temperature studied (i.e., 543 K). According to UV-vis absorbance results (350–450 nm),<sup>28</sup> soluble polymers can be produced from the decomposition of F at these experimental condition.

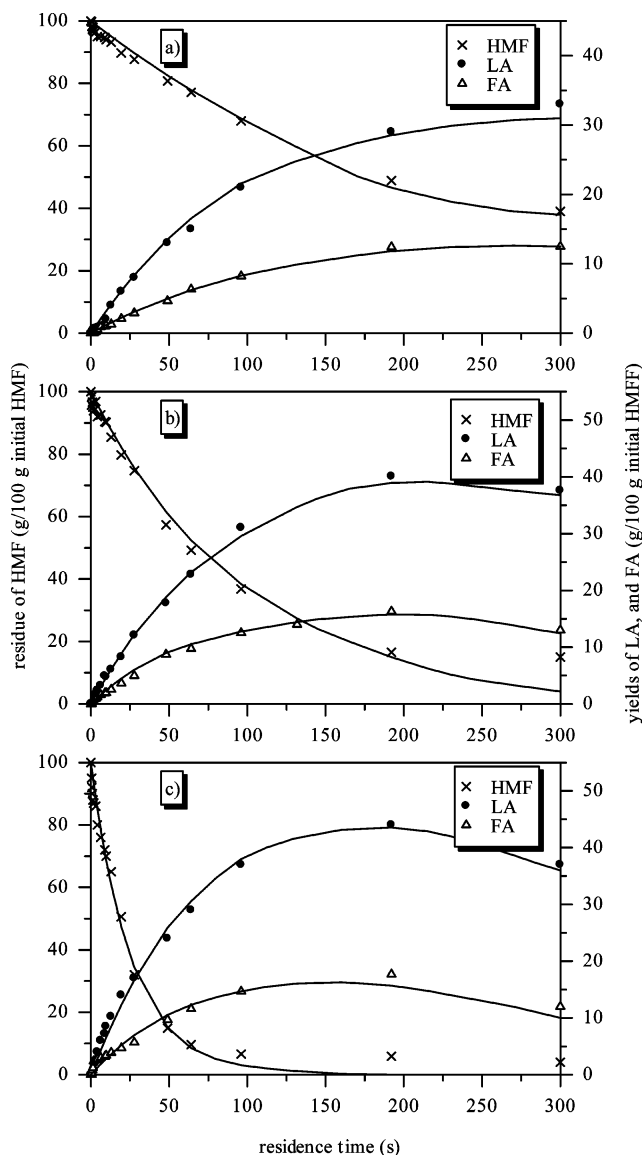
**3.4.2. Decomposition of HMF.** To make the kinetics of sub-CW reaction clear, we used HMF as the starting material. Experimental results showed the possibility of the decomposition of HMF as the substrate at the working range of temperature and residence time (see parts a, b, and c of Figure 6). As



**Figure 5.** Acid-catalyzed (initial pH 1.8 using HCl) dehydration of F in flow-type sub-CW at (a) 483, (b) 513, and (c) 543 K, at a pressure of 4 MPa; curves are theoretical lines calculated from the proposed kinetic model.

expected, the decomposition of HMF and the formation of LA and FA (and its rehydration products) increased with both increasing temperature and residence time. No 2FA (2-furfuraldehyde) was detected using HMF as a pure substrate. It can be concluded that 2FA can be obtained only from the decomposition of F. Parallel to the formation of HMF, 2-hydroxyacetyl-furan as an intermediate compound was formed via the decomposition of saccharides in the presence of HCl, which further contributes to the formation of soluble polymers.<sup>19</sup> In our previous work,<sup>11</sup> in the decomposition of saccharides at sub-CW conditions, the overall carbon balance showed no deficit and accounted for >99% of the initial amount of carbon. No inorganic carbon was detected. However, the total identified compounds were less than initial saccharides (based on mass balance). Therefore, as reported by other researchers, this deficit can be attributed to the formation of soluble polymers. On the other hand, in these works, water-soluble polymers were identified from the decomposition of HMF (as the starting material). In the present study, we found that it is possible to



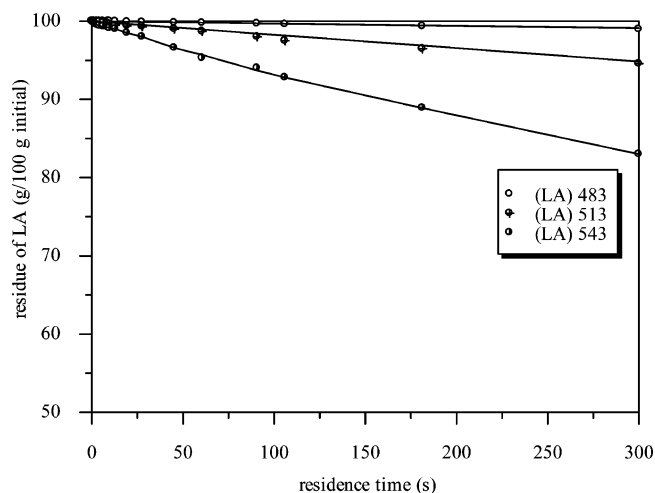


**Figure 6.** Acid-catalyzed (initial pH 1.8 using HCl) rehydration of HMF in flow-type sub-CW at (a) 483, (b) 513, and (c) 543 K, at a pressure of 4 MPa; curves are theoretical lines calculated from the proposed kinetic model.

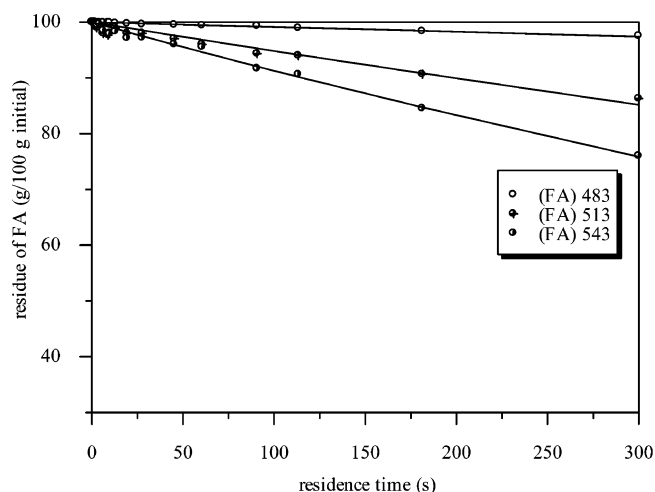
form these polymers from both saccharides and HMF using sub-CW. Therefore, we divided the soluble polymers based on the source of production.

**3.4.3. Decomposition of LA and FA.** To make the kinetics of the sub-CW reaction clear, we used HMF as the starting material. Although LA and FA also may slightly decompose in acidified sub-CW to other soluble compounds, we did not identify these decomposition products in this study (Figures 7 and 8). As shown in the figures, the decomposition of both LA and FA increased by residence time in the reaction temperature. We did not identify any absorbance at the range of 350 to 450 nm that is attributed to soluble polymers; therefore, LA and FA could not be the source of soluble polymers.

**3.5. Kinetic Modeling.** A simplified pathway for the decomposition of F has been proposed and is shown in Scheme 2. This reaction pathway shows F as a starting material; however, other monosaccharides may also be used instead of F. This pathway includes consecutive and concurrent reaction pathways that include the formation of HMF from the dehydration of F, the decomposition of F to 2FA, the rehydration of HMF to LA and FA, and the decomposition of LA and FA, with the formation of soluble polymers from both F and HMF.

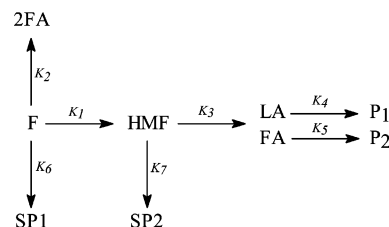


**Figure 7.** Acid-catalyzed (initial pH 1.8 using HCl) decomposition of LA in flow-type sub-CW at 483, 513, and 543 K, at a pressure of 4 MPa; curves are theoretical lines calculated from the proposed kinetic model.



**Figure 8.** Acid-catalyzed (initial pH 1.8 using HCl) decomposition of FA in flow-type sub-CW at 483, 513, and 543 K, at a pressure of 4 MPa; curves are theoretical lines calculated from the proposed kinetic model.

**Scheme 2. Proposed reaction pathway elucidated for F (HMF, LA, and or FA) decomposition in sub-CW. P1 and P2 are unknown decomposition products of LA and FA, respectively**



As shown in Scheme 2, we distinguished between polymers formed from F and HMF (SP1 and SP2, respectively). In the proposed model, because of rehydration of 1 mol of HMF to equimolar amounts of LA and FA, the formation rate constants of LA and FA were set as equal (that is,  $k_3$ ).

Basic assumptions in developing the kinetic model were demonstrated as follows: (i) all reactions identified were irreversible; (ii) negligible amounts of minor byproducts were not included in this model; and (iii) 2FA and soluble polymers did not undergo further decomposition reactions. In fact, the decomposition and formation of these polymers is poorly understood.<sup>32</sup> (It is obvious that 2FA as aldehyde easily

**Table 2. (a) Reaction Rate Equations and Their Analytical Solutions of Proposed Model Starting from F; (b) Reaction Rate Equations and Their Analytical Solutions of Proposed Model Starting from HMF; (c) Reaction Rate Equations and Their Analytical Solutions of Proposed Model Starting from LA and/or FA**

Part a		
eq	rate equation, F as substrate	analytical solution
2 <sup>a</sup>	$r_F = (d[F])/(d\tau) = -k_f[F]$	$[F] = [F]_o e^{-k_f\tau}$
3	$r_{2FA} = (d[2FA])/(d\tau) = k_2[F] = k_2[F]_o e^{-k_f\tau}$	$[2FA] = (k_2[F]_o)/(k_f < \text{frx} > (1 - e^{-k_f\tau})$
4	$r_{SP_1} = (d[SP_1])/(d\tau) = k_6[F] = k_6[F]_o e^{-k_f\tau}$	$[SP_1] = (k_6[F]_o)/(k_f(1 - e^{-k_f\tau})$
5 <sup>b</sup>	$r_{HMF} = (d[HMF])/(d\tau) = k_1[F] - k_h[HMF]$	$[HMF] = [F]_o(k_1)/(k_h - k_1)(e^{-k_1\tau} - e^{-k_h\tau})$
6	$r_{LA} = (d[LA])/(d\tau) = k_3[HMF] - k_4[LA]$	$[LA] = e^{-k_4\tau}[(k_3[F]_o k_1)/(k_h - k_1)][(1/(k_4 - k_1)) e^{(k_4 - k_1)\tau} - (1/(k_4 - k_h)) e^{(k_4 - k_h)\tau}]$
7	$r_{FA} = (d[FA])/(d\tau) = k_3[HMF] - k_5[FA]$	$[FA] = e^{-k_5\tau}[(k_3[F]_o k_1)/(k_h - k_1)][(1/(k_5 - k_1)) e^{(k_5 - k_1)\tau} - (1/(k_5 - k_h)) e^{(k_5 - k_h)\tau}]$
8	$r_{SP_2} = (d[SP_2])/(d\tau) = k_7[HMF]$	$[SP_2] = (k_6[F]_o)/(k_h(k_h - k_1))(k_1 e^{-k_h\tau} - k_h e^{-k_1\tau})$
9 <sup>a</sup>	where:	
10 <sup>b</sup>	$k_1 + k_2 + k_6 = k_f$	
11	$k_3 + k_7 = k_h$	
	at $\tau = 0$ : $[F] = [F]_o$ ; and $[2FA]$ , $[HMF]$ , $[LA]$ , $[FA]$ , $[SP_1]$ , and $[SP_2] = 0$	
Part b		
eq	rate equation, HMF as substrate	analytical solution
12	$r_{HMF} = (d[HMF])/(d\tau) = -k_h[HMF]$	$[HMF] = [HMF]_o e^{-k_h\tau}$
13 <sup>c</sup>	$r_{SP_2}(d[SP_2])/(d\tau) = k_7[HMF] = k_7[HMF]_o e^{-k_h\tau}$	$[SP_2] = (k_7[HMF]_o)/(k_h(1 - e^{-k_h\tau})$
14	$r_{LA} = (d[LA])/(d\tau) = k_3[HMF] - k_4[LA]$	$[LA] = ([HMF]_o k_3)/(k_4 - k_3)(e^{-k_3\tau} - e^{-k_4\tau})$
15	$r_{FA} = (d[FA])/(d\tau) = k_3[HMF] - k_5[FA]$	$[FA] = ((([HMF]_o k_3)/(k_5 - k_3))(e^{-k_3\tau} - e^{-k_5\tau})$
16 <sup>c</sup>	where:	
17	$k_3 + k_7 = k_h$	
	at $\tau = 0$ : $[HMF] = [HMF]_o$ ; and $[2FA]$ , $[LA]$ , $[FA]$ , and $[SP_2] = 0$	
Part c		
eq	rate equation, LA and or FA as substrate	analytical solution
18	$r_{LA} = (d[LA])/(d\tau) = -k_4[LA]$	$[LA] = [LA]_o e^{-k_4\tau}$
19	$r_{FA} = (d[FA])/(d\tau) = -k_5[FA]$	$[FA] = [FA]_o e^{-k_5\tau}$
20	where:	
	at $\tau = 0$ : $[LA] = [LA]_o$ and $[FA] = [FA]_o$	

<sup>a</sup>  $k_f$  is overall decomposition rate constant of F. <sup>b</sup>  $k_h$  overall decomposition rate constant of HMF, starting from F. <sup>c</sup>  $k_h$  overall decomposition rate constant of HMF, starting from HMF.

decomposes in sub-CW; however, in order to avoid complication, we simply assumed no decomposition reactions for 2FA.)

Only a part of this model is applicable for the decomposition of HMF, LA, and/or FA as starting materials. Starting from F, HMF is assumed as a detectable intermediate. The rate of formation of HMF must be faster than the decomposition rate of HMF; i.e., the conversion rate of HMF to LA and FA must be slower than the conversion rate of F to HMF.

By assuming that the rate law was first order with respect to each of the starting substrates, based on the reaction pathway proposed in Scheme 2, the differential rate equations were formulated and listed in Table 2 (parts a, b, and c). Equations 12–15 in Table 2b and eqs 18 and 19 in Table 2c show the variation of the yields of HMF, LA (and FA), and their decomposition products with reaction time, respectively.

Analytical solutions of the differential equations were obtained using the initial conditions (eqs 11, 17, and 20) and are listed in the right side of Table 2 (parts a, b, and c). The  $k_i$  values were determined by matching the experimental data by nonlinear least-squares curve-fitting method (Datafit Ver. 8.1, Oakdale Engineering, U.S.A.). Details about data analysis can be found in the literature.<sup>33</sup>

Figures 5–8 show the comparison between the experimental data and the theoretical lines based on the above proposed model for the decomposition of F, HMF, LA, and FA at 483, 513, and 543 K as a function of residence time. The solid lines indicated the theoretical lines. The model calculations and the experimental data showed good agreement for all products and substrates. Only a small deviation was observed at longer residence times for HMF, starting from either F and/or HMF.

**Table 3. Estimated Rate Constants ( $s^{-1}$ ) for Acid-Catalyzed Decomposition of F, HMF, and LA and FA and Formation Products at Three Different Temperatures of 483, 513, and 543 K; Experiments Were Repeated in Triplicate**

temp. (K)	substrate					
	F	( $s^{-1}$ )	HMF	( $s^{-1}$ )	LA and/or FA	( $s^{-1}$ )
483	$k_1$	$4.53 \times 10^{-3}$				
	$k_2$	$5.12 \times 10^{-4}$				
	$k_3$	$3.01 \times 10^{-3}$	$k_3$	$3.32 \times 10^{-3}$		
	$k_4$	$3.18 \times 10^{-5}$	$k_4$	$3.18 \times 10^{-5}$	$k_4$	$3.18 \times 10^{-5}$
	$k_5$	$8.30 \times 10^{-5}$	$k_5$	$8.30 \times 10^{-5}$	$k_5$	$8.30 \times 10^{-5}$
	$k_6$	$1.02 \times 10^{-1}$				
	$k_7$	$5.03 \times 10^{-5}$	$k_7$	$5.03 \times 10^{-5}$		
513	$k_1$	$9.05 \times 10^{-2}$				
	$k_2$	$4.83 \times 10^{-3}$				
	$k_3$	$9.90 \times 10^{-3}$	$k_3$	$9.81 \times 10^{-3}$		
	$k_4$	$1.78 \times 10^{-4}$	$k_4$	$1.78 \times 10^{-4}$	$k_4$	$1.78 \times 10^{-4}$
	$k_5$	$5.09 \times 10^{-4}$	$k_5$	$5.09 \times 10^{-4}$	$k_5$	$5.09 \times 10^{-4}$
	$k_6$	$3.06 \times 10^{-1}$				
	$k_7$	$2.68 \times 10^{-4}$	$k_7$	$2.68 \times 10^{-4}$		
543	$k_1$	$3.63 \times 10^{-1}$				
	$k_2$	$1.95 \times 10^{-2}$				
	$k_3$	$4.42 \times 10^{-2}$	$k_3$	$4.46 \times 10^{-2}$		
	$k_4$	$6.07 \times 10^{-4}$	$k_4$	$6.07 \times 10^{-4}$	$k_4$	$6.07 \times 10^{-4}$
	$k_5$	$9.07 \times 10^{-4}$	$k_5$	$9.07 \times 10^{-4}$	$k_5$	$9.07 \times 10^{-4}$
	$k_6$	1.77				
	$k_7$	$1.91 \times 10^{-3}$	$k_7$	$1.91 \times 10^{-3}$		

This may be caused by the additional interaction of the soluble polymers with HMF.<sup>19</sup>

Table 3 shows rate constants ( $k_i$ ) determined as mentioned above by successive steps. From the results obtained for LA and FA, the rate constants of  $k_4$  and  $k_5$  were determined by matching the data. Then, these two rate constants were used to

**Table 4. Activation Energies Calculated from Slope of Arrhenius Plots for the Proposed Kinetic Model**

substrate	activation energies (kJ/mol) for the reaction with rate constant of						
	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$	$k_7$
F	160.6	132.2	97.2	121.3	109.8	101.9	108.1
HMF			94.1	110.7	99.9		121.5
LA				107.9			
FA					102.3		
average	160.6	132.2	95.6	113.3	104.0	101.9	114.8

calculate  $k_3$  and  $k_7$ . Later, rate constants for F were estimated by using the rate constants that were obtained from the decomposition of HMF, LA, and FA.  $k_6$  (formation of SP1) is the largest one, and it increases with increasing temperature. In fact, there is a competition reaction between the production of HMF and the polymerization reactions (formation of SP1).<sup>34</sup> Therefore, the larger the amount of SP1, the smaller are the amounts of rehydration and dehydration products and vice versa. HMF produced from the dehydration of F is also polymerized to SP2; however, calculations show that the formation of SP2 is much smaller than that of SP1 ( $k_6 \gg k_7$ ).

As noted previously, HMF can also be polymerized to SP2. The formation rate constants of SP2,  $k_7$ , without concerning the initial feed (i.e., F or HMF), are almost the same (Table 3).

The rate constants of LA and FA exhibit no difference whether starting from F, HMF, and/or LA and FA. It can be concluded that there was no interaction on the decomposition of LA and FA from the other compounds that existed in the reaction media. FA decomposed faster than LA under the experimental conditions.

As a result, we calculated the rate constants for all reaction components; by using this model, the concentration profiles of SP1 and SP2, which cannot be quantified experimentally, can be individually predicted.

**3.6. Temperature Dependence of Rate Constants.** The rate constants  $k_i$  were affected by the temperature (Table 3) and could be represented by the Arrhenius equation. The plot of  $\ln k$  vs  $1/RT$  showed straight lines, with a slope of  $-E_a$ . These results showed that the rate constants increase with the reaction temperature, obeying the Arrhenius equation. It can be concluded that  $E_a$  of the reacted compounds were not temperature dependent based on the linearity of the lines. The activation energies of the reactions with rate constants from  $k_1$  to  $k_7$  along with the average activation energies (without concern for the kind of substrate) were calculated for the reactions and are listed in Table 4. Small variations of activation energies with substrates may result from experimental error.

**3.7. Effect of Acids on the Corrosion of sub-CW Pipes.** It is well-known that piping corrosion occurs in the presence of HCl at higher temperatures. In this study, as mentioned before, HCl was used as the acid catalyst. By analysis of the aqueous phase, after sub-CW treatment, Fe ions were identified, the amount of which was in direct relation with the amount of corrosion of the reactors. The concentrations of Fe ions were a function of residence times; for the shortest residence time (i.e., 0.5 s), Fe ions were identified at 0.21 ppm, which almost linearly increased by residence time up to 73 ppm at 300 s.

## 4. Conclusion

Decomposition of F (HMF, LA, and FA) was conducted in sub-CW at a temperature range of 483–543 K and a pressure of 4 MPa in the presence of HCl. The pressure had no effect on the decomposition reactions compared to the other operating

variables. Starting from F as the substrate, at higher acidic pH, LA (and FA), and at lower acidic pH, HMF, was obtained as the main product. Other major decomposition products were found as 2FA and soluble polymers. From the decomposition of HMF, the products were obtained as LA, FA, and soluble polymers; from the decomposition of LA and/or FA, we did not identify any decomposition products; however, it was realized that soluble polymers cannot be produced from LA and/or FA. 2FA was found to be produced only from F and not from HMF.

A simplified reaction pathway was proposed. On the basis of the experimental data obtained from the decomposition products, a kinetic model, in which all identified pathways were taken into consideration, was developed. This model distinguished between two different soluble polymers based on the source of production. Theoretical lines matched well with the experimental decomposition and formation curves of F, 2FA, HMF, LA, and FA. The best-fit parameters were determined by nonlinear regression analysis. The kinetic model can accurately predict the rate constant of F as well as other decomposition products, especially of SP1 and SP2, which cannot be quantified experimentally. The measured rate constants showed Arrhenius behavior in the experimental temperature range.

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