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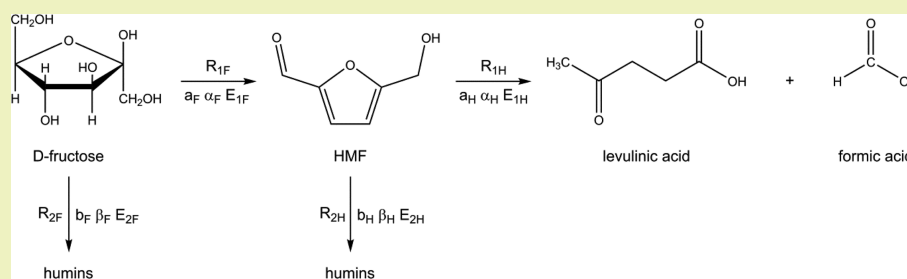
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## Experimental and Kinetic Modeling Studies on the Sulfuric Acid Catalyzed Conversion of D-Fructose to 5-Hydroxymethylfurfural and Levulinic Acid in Water

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## Supporting Information



**ABSTRACT:** Levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) have been identified as promising biomass-derived platform chemicals. A kinetic study on the conversion of D-fructose to HMF and LA in water using sulfuric acid as the catalyst has been performed in batch setups. The experiments were carried out in a temperature window of 140–180 °C, using sulfuric acid as the catalyst (0.005–1 M) and an initial D-fructose concentration between 0.1 and 1 M. A kinetic model for the conversion of D-fructose to HMF and the subsequent reaction of HMF to LA was developed including the kinetics for the formation of solid byproducts (humins) using a power-law approach. According to the model, the maximum attainable HMF yield in the experimental window is 56 mol % ( $C_{\text{fruc}} = 0.1$  M;  $C_{\text{acid}} = 0.005$  M; 166 °C), which is close to the highest experimental value within the range (53 mol %) and considerably higher than that reported for D-glucose. The highest modeled LA yield was 70 mol % ( $C_{\text{fruc}} = 0.1$  M;  $C_{\text{acid}} = 1$  M; 140 °C), close to the experimental value of 74 mol %. This LA yield is considerably higher than that found for D-glucose within the range of experimental conditions. The model was used to determine the optimum reactor configuration for highest HMF and LA yields, and it is shown that highest HMF yields are attainable in a PFR reactor, whereas a large extent of backmixing is favorable when aiming for a high LA yield.

**KEYWORDS:** D-Fructose, HMF, Levulinic acid, Kinetic modeling

## INTRODUCTION

The steady growth of the use of fossil resources has led to higher prices for fossil energy, fuels and petrochemical products as well as environmental concerns related to CO<sub>2</sub> emissions. As a result, the use of renewables is receiving high attention.<sup>1–10</sup> Biomass is considered a very attractive renewable source for the production of bioenergy, biofuels and biobased chemicals. Biomass is produced at an estimated rate of 170 billion metric tons per year by photosynthesis, though only 3–4% is used by humans for food- and nonfood applications.<sup>11–14</sup>

Lignocellulosic biomass is an interesting source for five-carbon sugars (D-xylose and L-arabinose) and six-carbon sugars (like D-glucose, D-mannose, D-fructose, and D-galactose) that can be converted into several interesting platform chemicals.<sup>2,11,13</sup> 5-Hydroxymethylfurfural (HMF) and levulinic acid (LA) have been identified as very attractive platform chemicals derived from C6 sugars. Both HMF and LA may be converted to a wide range

of derivatives with a broad application range (Figure S1, Supporting Information).<sup>2,3,10,15,16</sup>

HMF and LA are accessible from the C6 sugars in lignocellulosic biomass by an acid-catalyzed dehydration process. In the first step, the hexoses are dehydrated to HMF, which may react further to form LA together with formic acid (FA). The simplified reaction scheme is depicted in Scheme 1.

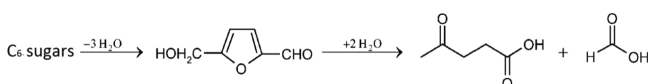
A wide range of catalysts (both homogeneous and heterogeneous), solvents, and solvent combinations have been explored and reviewed.<sup>5–7,17,18</sup> As part of a larger program to determine the kinetics of the individual steps in the conversion of C6 sugars to HMF/LA to be used as input for the development of efficient reactor configurations, we here report a kinetic study

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### Scheme 1. Simplified Reaction Scheme for the Conversion of C6 Sugars to HMF and LA and FA



on the conversion of D-fructose to LA and HMF using sulfuric acid as the catalyst.

A kinetic study with sulfuric acid is highly relevant, as this acid is an important catalyst for the conversion of C6 sugars to HMF and LA and actually most processes reported in the literature beyond batch studies in the lab use this catalyst (e.g., biofine process for LA).<sup>5,6,16</sup> It is also known that the kinetics of these processes in water are not solely described by the Brønsted acidity and that other effects (e.g., anion effects) play a role as well.<sup>5,6,19</sup> Thus, for scale up studies (e.g., reactor design), the kinetics for this particular acid needs to be known and this paper as such contributes to the field.

D-Fructose is, though it is more expensive than D-glucose, the preferred C6 sugar for HMF synthesis as the yields are at least 5 times higher than for D-glucose.<sup>5</sup> Our interest is in the use of water as the reaction medium and a simple, cheap, recyclable inorganic acid as the catalyst.

Kinetic studies on the conversion of D-fructose to HMF and LA in monophasic solvents (water, methanol, acetone/water, acetic acid) using soluble, inorganic Brønsted acids have been reported and relevant studies are summarized in Table 1.

On the basis of this overview, it can be concluded that detailed kinetic studies on the conversion of D-fructose to HMF and the subsequent reaction of HMF to LA using sulfuric acid in water as the solvent have not been reported to date. In this paper, a kinetic study on the conversion of D-fructose to HMF and LA in water using sulfuric acid including the rate of byproduct formation for a range of process conditions is reported using a power-law approach instead of assuming first-order reactions. With this model, optimal reaction conditions and reactor configurations can be determined to (i) increase the space time yields (kg product/(m<sup>3</sup>s)) and thus to reduce the reactor size for a given production capacity and (ii) optimize the yields of HMF and/or LA from D-fructose.

## EXPERIMENTAL SECTION

**Chemicals.** D-Fructose (99%) and LA (≥97%) were purchased from Acros Organic (Geel, Belgium). Sulfuric acid (96–98 wt %) and formic acid were purchased from Merck KGaA (Darmstadt, Germany). HMF was obtained from Sigma-Aldrich (Steinheim, Germany). All chemicals were used without further purification. For all experiments, deionized water was used to prepare the solutions.

**Experimental Procedures.** The experimental methods are based on published work by Girisuta et al.<sup>26</sup> The reactions were performed in small glass ampules with an inside diameter of 3 mm, a wall thickness of

1.5 mm, and length of 15 cm. The ampules were filled with approximately 0.5 mL of reaction mixture and then sealed by a torch. The ampules were placed in an aluminum rack that can hold up to 20 ampules. The rack was placed inside a convection oven held at a constant temperature (±1 °C).

At predetermined reaction times, ampules were taken from the oven and immediately submerged in a cold water bath to quench the reaction. The ampules were opened and the liquid products collected. Before analysis, the solids were separated from the liquid by centrifugation using a microcentrifuge (Omnilab International BV, 10–20 min at 1200 rpm). A sample of the clear solution was diluted with water and analyzed by HPLC.

**Analytical Methods.** High performance liquid chromatography (HPLC) was used to determine the concentration of products in the liquid phase. The HPLC system consisted of a Hewlett-Packard 1050 pump, a Bio-Rad organic acid column (Aminex HPX-87H), and a Waters 410 differential refractive index detector. Dilute sulfuric acid (5 mM) was used as the eluent at a flow rate of 0.55 cm<sup>3</sup> min<sup>-1</sup>. The column was operated at 60 °C. The analysis time for each sample was typically 45 min. The HPLC was calibrated with solutions of compounds with known concentrations.

**Definitions and Determination of the Kinetic Parameters.** The concentrations of the relevant compounds were determined by HPLC. These concentrations were used to calculate the conversion of D-fructose ( $X_{\text{FRC}}$ ), the yield of HMF ( $Y_{\text{HMF}}$ ), LA ( $Y_{\text{LA}}$ ), and FA ( $Y_{\text{FA}}$ ) according to the following equations:

$$X_{\text{FRC}} = \frac{(C_{\text{FRC},0} - C_{\text{FRC}})}{C_{\text{FRC},0}} \quad (1)$$

$$Y_{\text{HMF}} = \frac{(C_{\text{HMF}} - C_{\text{HMF},0})}{C_{\text{FRC},0}} \quad (2)$$

$$Y_{\text{LA}} = \frac{(C_{\text{LA}} - C_{\text{LA},0})}{C_{\text{FRC},0}} \quad (3)$$

$$Y_{\text{FA}} = \frac{(C_{\text{FA}} - C_{\text{FA},0})}{C_{\text{FRC},0}} \quad (4)$$

The space time yields (STY) for reactions in the batch reactor were calculated using

$$\text{STY} = \frac{C_{\text{FRC},0} X_{\text{FRC}}}{t} \quad (5)$$

where  $t$  is the batchtime.

Kinetic parameters for the reactions were determined using the software package MATLAB. A maximum-likelihood approach, based on minimization of errors between the experimental data and kinetic model was applied. To minimize the error between the measured values and the model, the Lsqnonlin method was used.

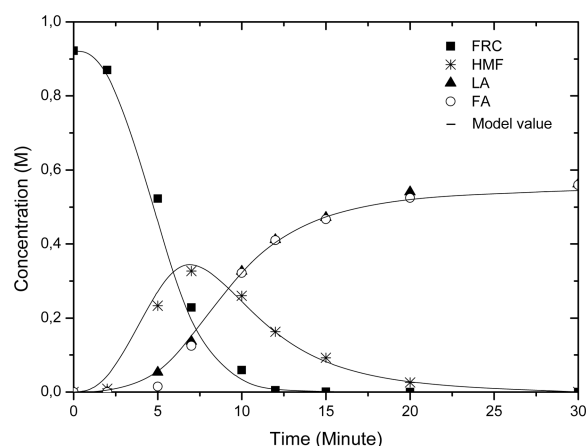
## RESULTS AND DISCUSSION

A total of 23 batch experiments was performed in a temperature range of 140–180 °C, initial D-fructose concentrations between

**Table 1. Overview of Kinetic Studies on D-Fructose Conversion to HMF and LA Using Inorganic Brønsted Acids in Water and/or Organic Solvents**

$C_{\text{FRC},0}$	$T, ^\circ\text{C}$	acid	solvent	ref
0.25–1 M	95	HCl (0.5–2 M)	water	17
0.05–0.1 M	210–270	HCl (0.016 M)	water	21
0.03 M	210–270	HCl, pH = 1.8	water	21
5–20%w/v	70–150	HCl, (2.5–10%w/v)	water	22
0.06 M	120–270	H <sub>2</sub> SO <sub>4</sub> (10 mM)	methanol	23
0.2–1 M	170–220	H <sub>3</sub> PO <sub>4</sub> (0.1–0.5 M)	MIBK–water	24
0.05 M	180–300	H <sub>2</sub> SO <sub>4</sub> (5 mM)	acetone–water	25

0.1 and 1 M, and sulfuric acid concentrations between 0.005 and 1 M. A typical concentration versus time profile is shown in Figure 1. Three main products were observed: HMF as the intermediate and LA and FA as the final products.



**Figure 1.** Typical concentration profile for D-fructose ( $T = 140\text{ }^{\circ}\text{C}$ ,  $C_{\text{FRC},0} = 1\text{ M}$ ,  $C_{\text{H}_2\text{SO}_4} = 0.5\text{ M}$ ).

Some other byproducts were also detected in the liquid phase by HPLC (e.g., furfural and D-glucose). However, their peak areas were low and as such they were not quantified and further taken into account in the kinetic modeling. LA and FA were in most cases formed in a close to 1 to 1 molar ratio.

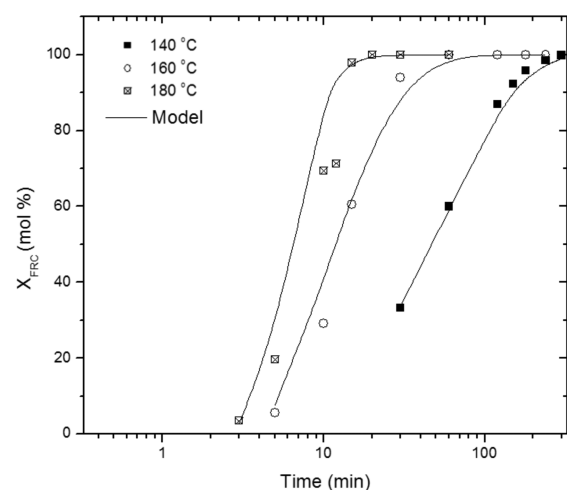
Insoluble byproducts known as humins were formed in all experiments, though the amount was more pronounced at prolonged reaction times. Elemental analysis on a representative humin sample showed the presence of 65.99 wt % of carbon, 4.55 wt % of hydrogen, and 29.46 wt % of oxygen. These values are well within the range for humins produced from C6 sugars (64–67 wt % carbon and 28–31 wt % oxygen).<sup>27</sup>

**Effect of Process Conditions on D-Fructose Conversion and Product Yields.** The effect of the temperature on the D-fructose conversion (initial D-fructose concentration 0.1 M, 0.01 M sulfuric acid) is given in Figure 2. As expected, the temperature has a profound effect on the reaction rates. Full D-fructose conversion is obtained after 15 min at 180 °C whereas it takes about 300 min at 140 °C.

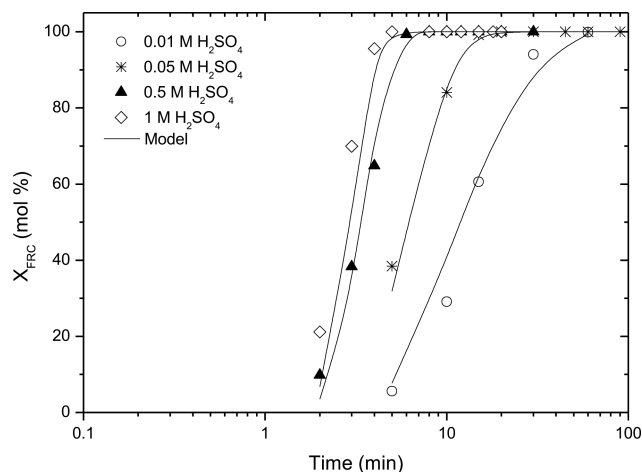
The effect of the initial D-fructose concentration on D-fructose conversion is given in Figure S2 (Supporting Information). The conversion is essentially independent of the loading, an indication that the order in D-fructose is close to one.

The effect of sulfuric acid concentrations on the D-fructose conversion is presented in Figure 3 and clearly implies that high acid concentrations lead to enhanced D-fructose conversion rates. For a first-order dependency of both acid and D-fructose, a plot of  $(\ln(1 - X_{\text{FRC}}))/C_{\text{H}^+}$  versus the time should give a straight line. This indeed proved to be the case for the data reported in Figure 3 ( $R^2 = 0.982$ , figure not shown for brevity) indicating that the order in acid is close to one.

The highest HMF yield within the experimental window was 53 mol %, obtained at an initial D-fructose concentration of 0.1 M, a sulfuric acid concentration of 0.01 M, and a temperature of 180 °C. The HMF yield is considerably higher than for D-glucose, for which Girisuta et al.<sup>26</sup> reported a maximum yield of 5 mol % in water using sulfuric acid as the catalyst in a similar window of process conditions. Thus, these findings support the general consensus in the literature that D-fructose is the preferred



**Figure 2.** Effect of temperature on D-fructose conversion ( $C_{\text{FRC},0} = 0.1\text{ M}$ ,  $C_{\text{H}_2\text{SO}_4} = 0.01\text{ M}$ ).



**Figure 3.** Effect of acid concentration on D-fructose conversion ( $T = 160\text{ }^{\circ}\text{C}$ ,  $C_{\text{FRC},0} = 0.1\text{ M}$ ).

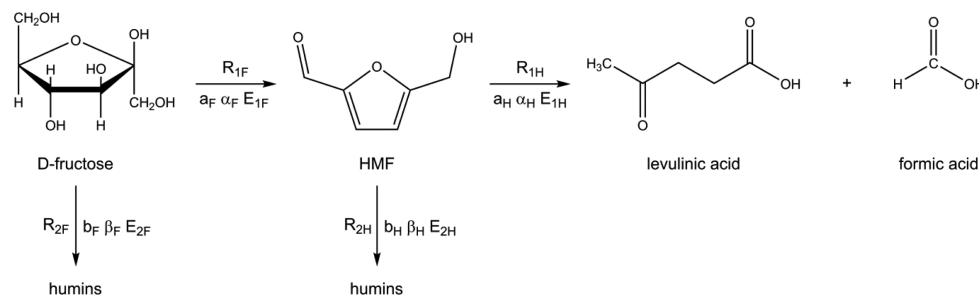
feedstock for HMF synthesis in water when using inorganic acids as the catalyst.<sup>5</sup>

For LA, the highest experimental yield (74 mol %) was found at a D-fructose concentration of 0.1 M, a sulfuric acid concentration of 1 M, and a temperature of 140 °C. These yields are much higher than found for D-glucose in water using sulfuric acid as the catalyst.<sup>26</sup> In the latter study, the highest LA yield within the process window was 60 mol % (140 °C;  $C_{\text{GLC},0} = 0.1\text{ M}$ ;  $C_{\text{acid}} = 1\text{ M}$ ). Thus, these findings indicate that D-fructose is a better source for LA synthesis than D-glucose when considering product yield. Detailed studies regarding LA synthesis from D-fructose are scarce, and the focus is mainly on the use of D-glucose. An overview of relevant studies for D-fructose conversion to LA in water using homogeneous and heterogeneous catalysts is provided in Table S1 (Supporting Information). Yields between 25 and 65 mol % have been reported, though a clear comparison with our results using sulfuric acid is cumbersome due to the differences in process conditions (e.g., temperature) and types of catalyst used.

**Kinetic Modeling. Model Development.** On the basis of the literature, the acid-catalyzed decomposition of D-fructose is expected to proceed according to a number of series-parallel reactions.<sup>5</sup> For simplification, it is assumed that the reaction



Scheme 2. Reaction Network for the Conversion of D-Fructose to HMF and LA As Used in the Kinetic Model



network involves the direct reaction of D-fructose to HMF, which subsequently reacts to LA and FA, though this is not necessarily the correct mechanism on a molecular level. These simplifications were included as the kinetic model would otherwise contain a large number of parameters, which limits the predictive value of the model. It is assumed that D-fructose and HMF also form humins, see Scheme 2 for details. A power-law modeling approach was used;<sup>26</sup> details regarding the kinetic expressions are given in the Supporting Information.

**Kinetic Modeling Results.** The results of a total of 23 batch experiments at various conditions were used to develop the kinetic model, with each experiment providing on average 24 data points (8 samples were taken during the batch time and the concentrations of D-fructose, HMF, and LA were determined). The experiments were carried out at temperatures between 140 and 180 °C, initial D-fructose concentrations between 0.1 and 1 M, and sulfuric acid concentrations between 0.005 and 1 M.

The kinetic constants, orders in reactants and activation energies were determined using the MATLAB software package by simultaneous modeling of the complete data set. The results for the conversion of D-fructose to HMF and humins (Scheme 2) are given in Table 2 and in the Supporting Information (Table S2).

Table 2. Kinetic Parameters for D-Fructose Conversion to HMF and Humins Using H<sub>2</sub>SO<sub>4</sub>

parameters	value	units
$k_{1RF}$	$1.1 \pm 0.1$	$(M^{(1-a_F)}(-\alpha_F) \text{ min}^{-1})^a$
$E_{1F}$	$123 \pm 5$	$\text{kJ mol}^{-1}$
$k_{2RF}$	$0.55 \pm 0.1$	$(M^{(1-b_F)}(-\beta_F) \text{ min}^{-1})^a$
$E_{2F}$	$148 \pm 12$	$\text{kJ mol}^{-1}$
$a_F$	$1.006 \pm 0.003$	
$b_F$	$1.179 \pm 0.06$	
$\alpha_F$	$0.958 \pm 0.02$	
$\beta_F$	$1.056 \pm 0.06$	

<sup>a</sup> $T_R = 140$  °C.

The kinetic parameters for the reaction of HMF to LA and humins were initially taken from a previous study by Girisuta.<sup>19</sup> However, when these kinetic values were implemented, the model fit was below expectations. This can be due to slightly different experimental procedures or, alternatively, by different interactions of the starting C6 sugars (D-fructose and D-glucose) with intermediates, e.g., leading to humins. These interactions are currently not taken into account in the kinetic model. Therefore, the kinetic parameters for the reaction of HMF to LA and humins were determined independently using the experimental data set. The Girisuta data and the best fit values for the current data set are presented in Table 3.

Table 3. Kinetic Parameters Estimation for HMF Conversion to LA and FA

parameters	previous research <sup>19</sup>	this work	units
$k_{1RH}$	$0.34 \pm 0.01$	$0.38 \pm 0.04$	$(M^{(1-a_H)}(-\alpha_H) \text{ min}^{-1})^a$
$E_{1H}$	$110 \pm 0.7$	$92 \pm 5$	$\text{kJ mol}^{-1}$
$k_{2RH}$	$0.117 \pm 0.008$	$0.142 \pm 0.04$	$(M^{(1-b_H)}(-\beta_H) \text{ min}^{-1})^a$
$E_{2H}$	$111 \pm 2$	$119 \pm 10$	$\text{kJ mol}^{-1}$
$a_H$	$0.88 \pm 0.01$	$0.89 \pm 0.03$	
$b_H$	$1.23 \pm 0.03$	$1.21 \pm 0.08$	
$\alpha_H$	$1.38 \pm 0.02$	$1.16 \pm 0.02$	
$\beta_H$	$1.07 \pm 0.04$	$0.90 \pm 0.05$	

<sup>a</sup> $T_R = 140$  °C.

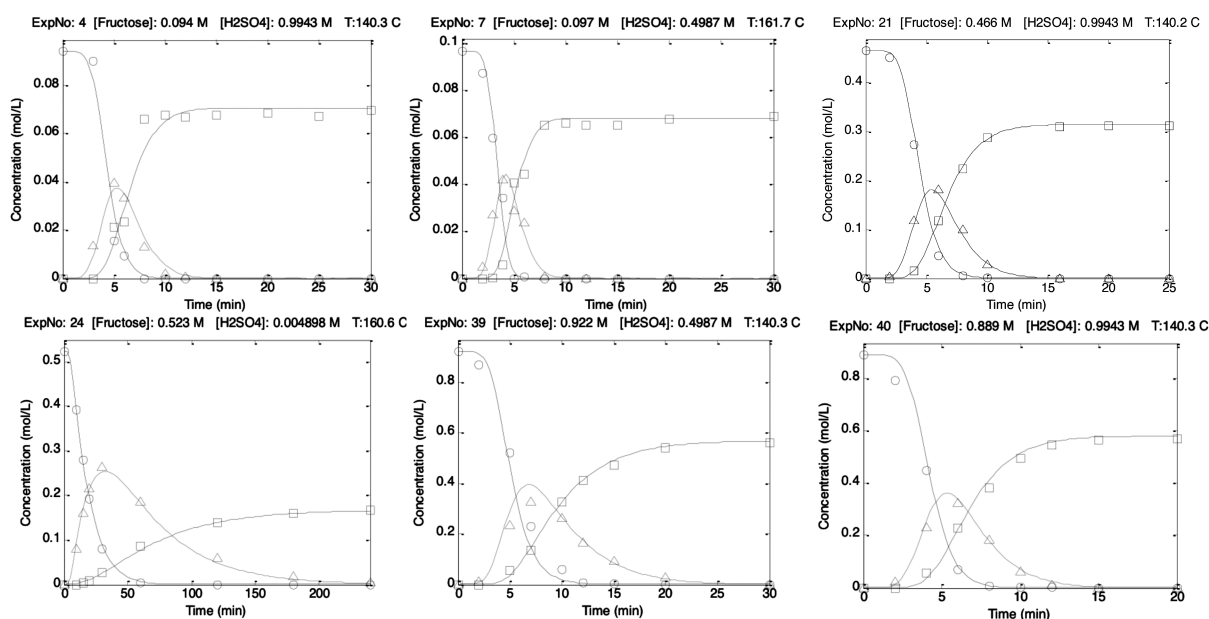
The values are in reasonable agreement, the main differences are the activation energy for the conversion of HMF to LA ( $E_{1H}$ ) and the orders in acid for LA and humin formation ( $\alpha_H$  and  $\beta_H$ ). Figure 4 and the parity plot in Figure S3 (Supporting Information) show that the fit between the model and the experimental values is good.

The order in D-fructose for the reaction to HMF was found to be close to one ( $1.006 \pm 0.003$ ), whereas the order was  $1.179 \pm 0.06$  for the reaction of D-fructose to humins. These findings are in line with the near independency of the D-fructose conversion of the initial D-fructose concentration (Figure S2, Supporting Information).

The acid dependency of the experimental D-fructose conversion versus batchtime profiles (Figure 3) indicates that the order in acid for the two reactions involving D-fructose (to HMF and to humins) should both be close to one and this was confirmed by the kinetic modeling activities ( $0.958 \pm 0.02$  and  $1.056 \pm 0.06$ ).

The activation energy for the reaction of D-fructose to HMF ( $R_{1F}$ ) was  $123 \pm 5$  kJ/mol. This value is lower than a previous study from our group for the reaction of D-glucose to HMF in water with sulfuric acid where an activation energy of 152 kJ/mol was reported using a power-law approach and a similar reaction network as that used here.<sup>26</sup> Thus, D-fructose appears to be more reactive than D-glucose (*vide infra*).

**Comparison of the Kinetic Models from the Modeling Activities with Literature Data.** It is of interest to compare the experimentally determined kinetic parameters and particularly the activation energy for the reaction of D-fructose to HMF in water with those reported for various catalysts in the literature. An overview is given in Table 4, where kinetic studies are compiled for reactions in water only using both soluble and solid Brønsted acid catalysts. As such, biphasic and water–organic solvent mixtures are not included in the analyses, as it is well-known that solvent effects play a major role in Brønsted acid-catalyzed reactions, making comparison difficult.



**Figure 4.** Comparison of experimental data (O, FRC; Δ, HMF; □, LA) and kinetic model (solid line) for various reaction conditions.

A number of studies have been reported using HCl as the catalyst. Kuster et al.<sup>17</sup> explored the kinetics of the conversion of D-fructose (0.25–1 M) to HMF in water using HCl as the catalyst (0.25–1 M) at a fixed temperature of 95 °C in a batch setup. The results were modeled using a mechanistic scheme involving the conversion of D-fructose to an intermediate (X) and subsequently to HMF. HMF is rehydrated via a second intermediate (Y) to give LA and FA. All four reactions were assumed to be first-order in substrate. In addition, both X and Y may also react to form humins, for which the order was a parameter of the kinetic model and found to be 1.3 for X.

Asghari et al.<sup>21</sup> investigated the kinetics of D-fructose conversion to HMF and LA at elevated temperatures (210–270 °C) in subcritical water using HCl as the catalyst. A reaction network was proposed including a number of reactions (e.g., to furfural) that are not occurring to a significant extent below 200 °C. For modeling purposes, experiments performed at a fixed HCl concentration (0.016 M) were used and as such the acid dependency was not taken into account.

Recently, Swift et al.<sup>22</sup> reported an extensive kinetic study on D-fructose (5–20%w/v) dehydration to HMF and the subsequent rehydration to LA at relatively low temperatures (70–150 °C) using HCl as the catalyst (pH: 0.7–1.6) in a batch setup. A reaction network was developed involving the five tautomeric forms of D-fructose. It is assumed that only the two furanose forms give HMF by a two-step reaction involving a reversible protonation step at the C2 position followed by an irreversible, kinetically controlled hydride shift (Scheme 3).

In addition, a separate reaction from D-fructose to FA and humins is incorporated to account for the observed deviation of the equimolar FA/LA ratio at low D-fructose conversions. Additional humin formation pathways include direct reactions starting from D-fructose and HMF. The proposed mechanism is given in Scheme 4. For modeling purposes, a reaction order of 1 was used for both HCl and D-fructose in all reactions. The conversion rate of D-fructose is thus equal to the sum of three individual reactions, the primary reaction to HMF via an intermediate, and two pathways leading to humin formation, of which one also forms FA.

Kinetic studies using organic acids (formic acid (FA) and acetic acid (AA)) have been reported by Li et al.<sup>28</sup> in subcritical water (180–220 °C, 100 bar) in a batch reactor. The reactions were modeled using a first-order approach.

Unfortunately, detailed kinetic studies for the conversion of D-fructose in water using sulfuric acid as the catalyst have not been reported to date. We have recently reported the activation energy for the decomposition of D-fructose in water using sulfuric acid as the catalyst as part of a larger study to assess the reactivity of a variety of C6 sugars.<sup>29</sup> However, only the rate of decomposition of D-fructose was determined, without considering any products in the kinetic analysis. The activation energy was found to be  $124 \pm 22$  kJ/mol.

Figure 5 presents an overview of the reported activation energies for the conversion of D-fructose to HMF for the kinetic studies reported in Table 4.

The reported activation energies for the conversion of D-fructose to HMF for soluble Brønsted acids in water are between 112 and 160 kJ/mol. The spread is much larger for the two heterogeneous Brønsted acids (66–135 kJ/mol), though it is difficult to draw sound conclusions from only two studies.

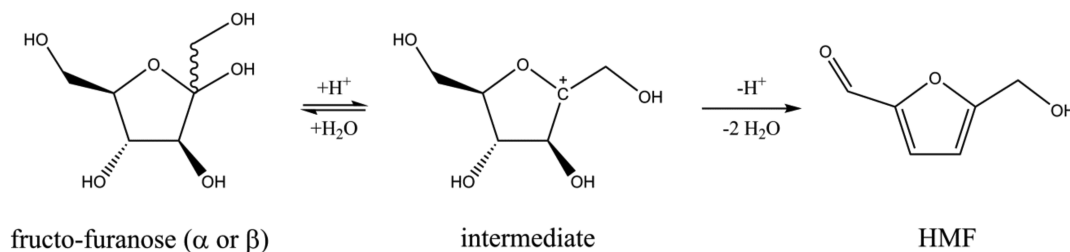
It is also cumbersome to conclude whether HCl or sulfuric acid is the best regarding catalyst performance, i.e., has the lowest activation energy. This is due to the differences in experimental conditions (temperature window, pressures (autogenous versus high pressure/subcritical regime)) and the proposed reaction network for the various studies. For instance, the activation energy for the first-order reaction of D-fructose to HMF using HCl, as reported by Asghari and Yoshida,<sup>21</sup> is higher (161 kJ/mol) than observed in this study with sulfuric acid (123.5 kJ/mol). However, (i) the temperature window is different (>210 °C versus max. 180 °C for this study) and (ii) a reaction model with three parallel reactions involving D-fructose was assumed by Asghari instead of the two in our study, and all three were reported to have different activation energies (101–161 kJ/mol).

Comparison of our value for the activation energy with the recently reported activation energy by Swift et al.<sup>22</sup> using HCl as the catalyst is also not straightforward, as a two-step dehydration mechanism is assumed by Swift et al. (Scheme 3). However, as

Table 4. Overview of Kinetic Studies on the Conversion of D-Fructose to HMF in Water

Scheme <sup>a</sup>	Catalyst	T (°C)	Kinetic expression	Activation energy (kJ/mol)	Ref.
<b>Homogenous Catalysts</b>					
$\begin{array}{c} \text{FRC} \xrightarrow{R_{1F}} \text{X} \xrightarrow{R_{1X}} \text{HMF} \xrightarrow{R_{1H}} \text{Y} \xrightarrow{R_{1Y}} \text{LA} + \text{FA} \\ \downarrow R_{2X} \qquad \qquad \downarrow R_{2Y} \\ \text{humins} \qquad \qquad \text{humins} \end{array}$	HCl	95	First order in D-fructose for $R_{1F}$ and $R_{1H}$	-	17
$\begin{array}{c} \text{FUR} \\ R_{2F} \uparrow \\ \text{FRC} \xrightarrow{R_{1F}} \text{HMF} \xrightarrow{R_{1H}} \text{LA} \rightarrow \text{P1} \\ \downarrow R_{3F} \qquad \downarrow R_{2H} \qquad \downarrow \\ \text{SP1} \qquad \text{SP2} \qquad \text{FA} \rightarrow \text{P1} \end{array}$	HCl	210-270, 40 – 150 bar	First order in D-fructose for all reactions involving D-fructose	$E_{R1F} = 160$ $E_{R2F} = 132$ $E_{R3F} = 102$	21
$\text{FRC} \xrightleftharpoons{K} \text{I} \xrightarrow{R_{1F}} \text{HMF}$	HCl	70-150	First order in D-fructose	$E_{1F} = 126 \pm 2$ $E_F = 130$ (150°C) <sup>b</sup>	22
$\text{FRC} \xrightarrow{R_F} \text{HMF}$	formic acid	180–220, 100 bar	First order in D-fructose	$E_{RF} = 112 \pm 13$	28
	acetic acid	180–220, 100 bar	First order in D-fructose	$E_{RF} = 125 \pm 13$	28
$\text{FRC} \xrightarrow{R_F} \text{HMF}$	H <sub>2</sub> SO <sub>4</sub>	100-160	First order in D-fructose	$E_{RF} = 124 \pm 22$	29
$\begin{array}{c} \text{FRC} \xrightarrow{R_{1F}} \text{HMF} \xrightarrow{R_{1H}} \text{LA} + \text{FA} \\ \downarrow R_{2F} \qquad \downarrow R_{2H} \\ \text{humins} \qquad \text{humins} \end{array}$	H <sub>2</sub> SO <sub>4</sub>	140–180	Power law model	$E_{R1F} = 123 \pm 5$	This paper
<b>Heterogeneous Catalysts</b>					
$\text{FRC} \xrightarrow{R_F} \text{HMF}$	NbOPO <sub>4</sub>	90 – 110	First order in D-fructose	$E_{RF} = 66 \pm 8$	30
$\text{FRC} \xrightarrow{R_1} \text{P}$	Activated carbon	160-220	Not reported	$E_{R1} = 135$	31

<sup>a</sup>Focus on the conversion of D-fructose to HMF; full model not given in all cases. <sup>b</sup>Apparent activation energy for the reaction  $\text{FRC} \rightarrow \text{HMF}$  including the temperature dependence of the pre-equilibrium reaction (Scheme 3).

Scheme 3. Proposed Two-Steps Dehydration Mechanism for Fructose to HMF<sup>22</sup>

the first step is an equilibrium reaction, the apparent activation energy of the two-step mechanism can be calculated using the temperature dependency of the first equilibrium constant and the

known activation energy of the second step. By using this approach, Swift et al. reported an activation energy of the HCl catalyzed conversion of D-fructose to HMF of 136 kJ/mol at 150

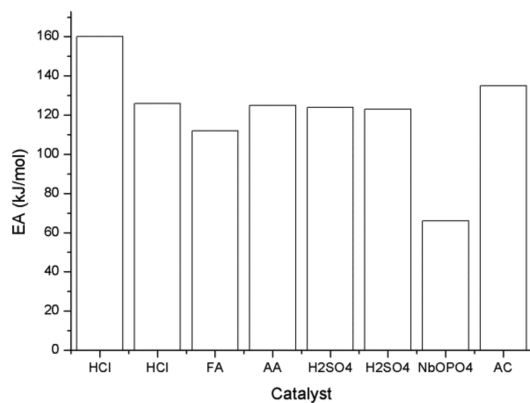
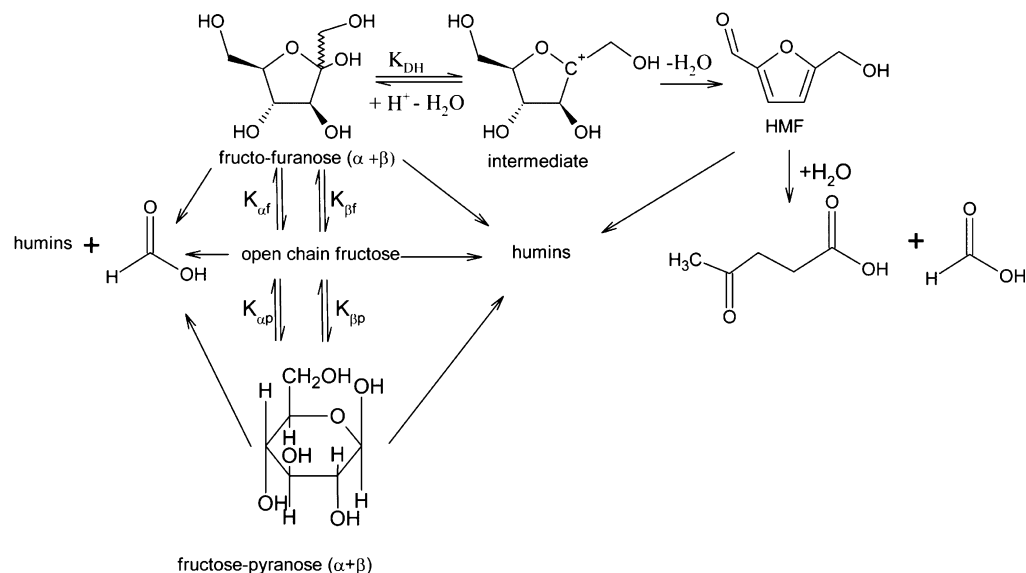
Scheme 4. Proposed Mechanism of the Acid-Catalyzed Dehydration of D-Fructose in Water<sup>22</sup>

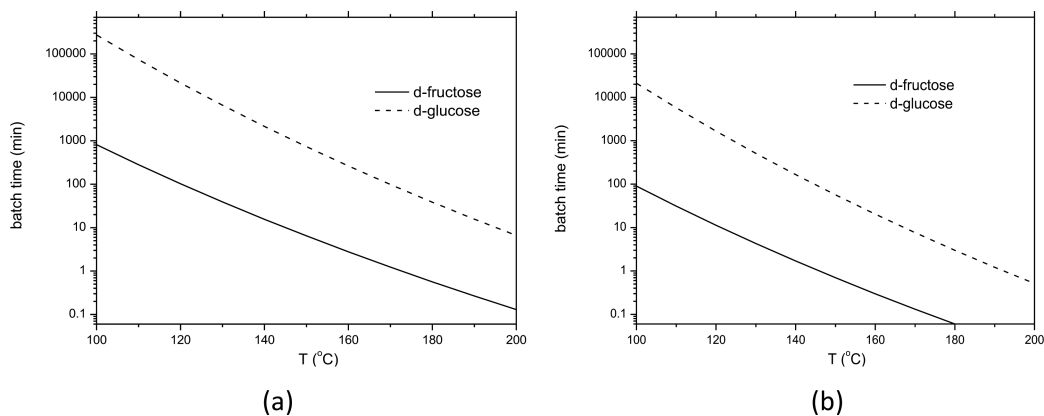
Figure 5. Activation energies for the conversion of D-fructose to HMF in water.

$^{\circ}\text{C}$ , which is slightly higher than found in this study for sulfuric acid. Thus, very tentatively, it appears that the activation energy for sulfuric acid for the reaction of D-fructose to HMF is slightly lower than for HCl. These findings are in line with studies from Wu et al.<sup>32</sup> on the reaction of D-fructose to HMF using inorganic

potassium salts. This study showed a clear anion effect and the reaction rates for the decomposition of D-fructose were higher for the sulfate anion than for the chloride anion. Such anion effects may also play a role in the strong acidic media used in our study, particularly when considering that the amount of  $\text{H}^+$  is essentially similar for very strong acids in water, like HCl and sulfuric acid.

**Model Implications for a Batch Reactor.** *D-Fructose Conversion Rates.* The kinetic model allows determination of the conversion of D-fructose and the yields of LA and HMF as a function of process conditions. As an example, the modeled batch time required for a D-fructose conversion of 90 mol % at different acid concentrations and temperatures is provided in Figure 6. In addition, the results were compared with those obtained for a kinetic model using D-glucose as the feed and sulfuric acid as the catalyst.<sup>26</sup>

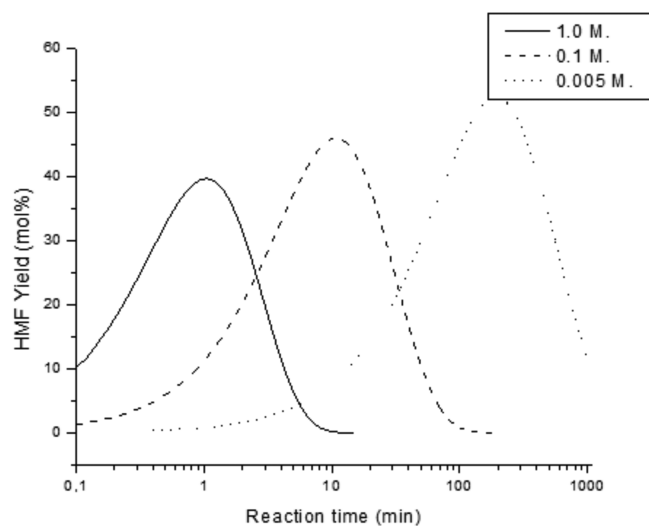
As anticipated, the batchtime is a strong function of the temperature, with times up to 1000 min at 100  $^{\circ}\text{C}$  versus less than 1 min at temperatures above 180  $^{\circ}\text{C}$  (0.1 M) to obtain 90% D-fructose conversion. For all temperatures and acid concentrations within the window, D-fructose is by far more reactive than D-glucose, and on average a factor of about 100 was calculated. The conversion rate increases when using higher acid

Figure 6. Required batch time for 90% of C6 sugar (D-fructose and D-glucose) conversion versus temperature for (a)  $\text{H}_2\text{SO}_4 = 0.1 \text{ M}$  and (b)  $\text{H}_2\text{SO}_4 = 1 \text{ M}$ .



concentrations (compare Figure 6a,b), as expected based on the positive and close to one order in acid in the kinetic model.

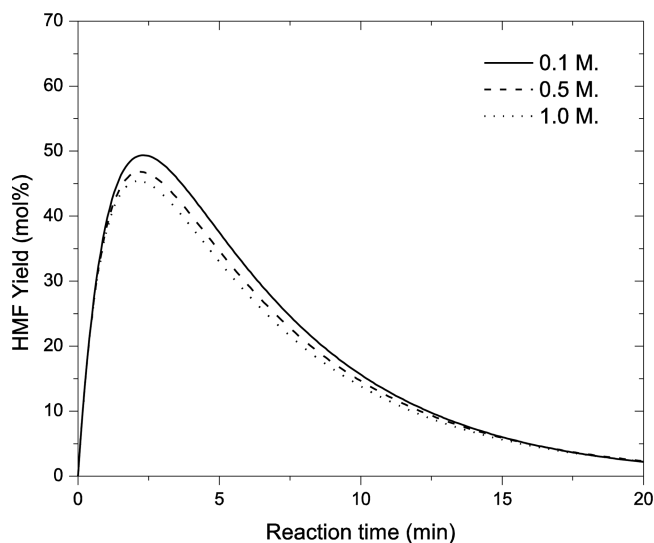
**Model Implications for HMF and LA Yield a Batch Reactor.** The highest yield of HMF within the experimental window was calculated and found to be 56 mol % at 166 °C, starting with 0.1 M D-fructose and a sulfuric acid concentration of 0.005 M. The model allows calculation of the HMF yields as a function of process conditions. The effect of the acid concentration on the yield of HMF ( $T = 140$  °C,  $C_{\text{FRC},0} = 0.5$  M) is given in Figure 7. The maximum achievable HMF yield is a



**Figure 7.** HMF yields versus time for different acid concentrations ( $T = 140$  °C,  $C_{\text{FRC},0} = 0.5$  M).

function of the acid concentration, with the lowest acid concentration (0.005 M) leading to the highest HMF yield. Clearly, this goes at the expense of reaction rates and the optimum at the lowest acid concentration is obtained after about 200 min of reaction time, compared to 1 min for the highest acid concentration in the range (1 M).

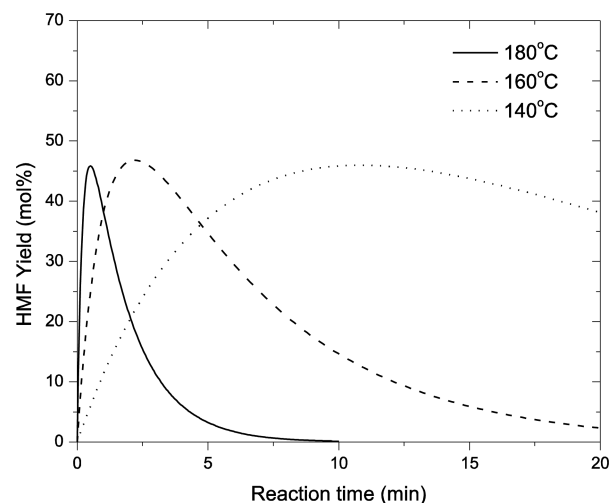
The HMF yield shows a minor dependence on the D-fructose loading, see Figure 8 for details, though a lower intake has a slight



**Figure 8.** HMF yields versus time for different initial D-fructose intakes ( $T = 160$  °C, acid concentration = 0.1 M).

beneficial effect (160 °C, acid concentration = 0.1 M). The main reason is a slightly higher order in the reactions leading to humins than the desired main reactions (Tables 2 and 3), indicating that humin formation is retarded at dilute conditions.

The effect of temperature on HMF yields within the temperature range 140–180 °C is relatively limited, see Figure 9 for details ( $C_{\text{FRC},0} = 0.5$  M,  $C_{\text{acid}} = 0.1$  M). These findings may

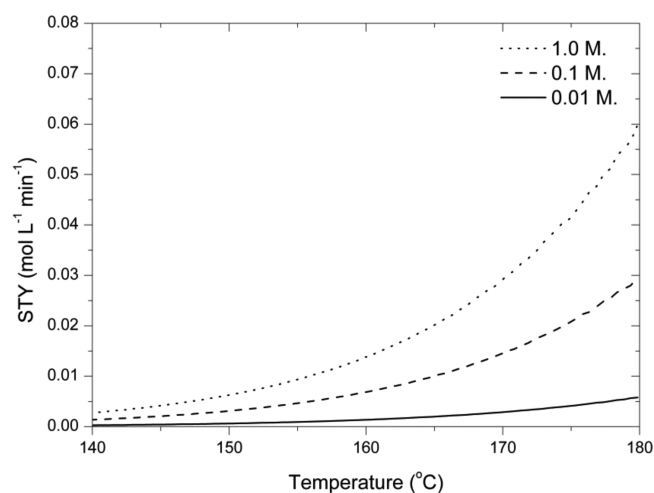


**Figure 9.** HMF yields versus time at different temperatures ( $C_{\text{FRC},0} = 0.5$  M, acid concentration = 0.1 M).

be explained by considering the differences in activation energy of the three main reactions with the highest kinetic constants at reference temperature ( $R_{1F}$ , D-fructose to HMF;  $R_{2F}$ , D-fructose to humins;  $R_{1H}$ , HMF to LA and FA). The activation energy for  $R_{2F}$  is the highest of the three ( $148 \pm 12$  kJ/mol) and as such humin formation would be expected to be favored at higher temperatures, leading to a lowering of the HMF yields. The reaction of HMF to LA has the lowest activation energy ( $92 \pm 5$  kJ/mol) and a lowering of the HMF yield is expected at lower temperatures. Apparently, both effects cancel out and a such the yield of HMF is about constant in the temperature range used in this study. These findings are not in agreement with the data reported by Swift et al.<sup>22</sup> for D-fructose with HCl as the catalyst. Here, the HMF yield is a strong function of the temperature, with higher temperatures leading to higher HMF yields. The maximum HMF yield at 150 °C (pH = 0.7) is about 46 mol %. Though comparison is difficult as the initial D-fructose concentration is not given, it is in the range as observed for sulfuric acid in our study. The reasons for this observed discrepancy in HMF yields versus temperatures between HCl and sulfuric acid may be due to the difference in temperature window for both studies (70–150 °C for HCl versus 140–180 °C for sulfuric acid)<sup>22</sup> and possible anion effects. Extended studies in the same temperature window will be required to draw definite conclusions.

**Model Predictions for the Space Time Yield (STY) of HMF.** The STY, also known as the volumetric production rate (mol product/(reactor volume-time)), is an important parameter for process optimization. A high STY is beneficial, as it allows for a reduction of the reactor size for a given production capacity, leading to lower investment costs. Calculation details regarding the STY are given in the Supporting Information. The highest STY as a function of the temperature and the initial D-fructose concentration (0.01–1 M) at a fixed acid concentration of 0.005

M is given in Figure 10. The highest STY (combination of highest HMF yield and reaction rate) is found at the highest

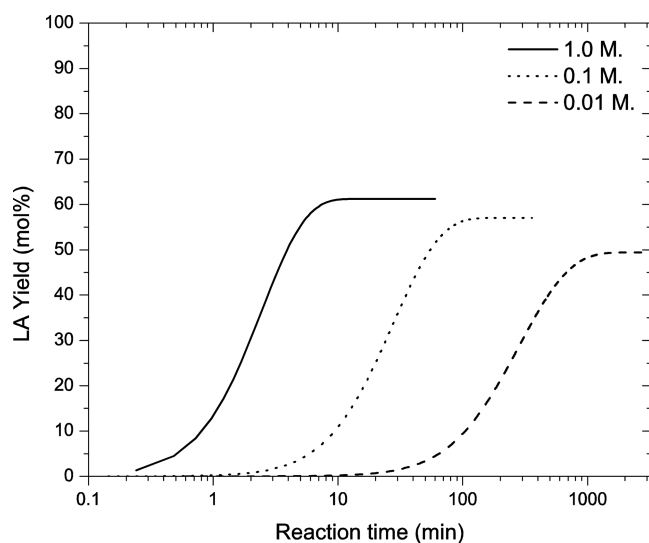


**Figure 10.** STY of HMF versus temperature and initial D-fructose concentration (acid concentration = 0.005 M).

temperature (180 °C) and highest initial D-fructose concentrations (1 M) within the experimental window.

**Model Predictions for LA Yield.** The model not only allows for determination of the HMF yield and STY versus process conditions but may also be used for a similar analyses for LA. The highest modeled LA yield was 70 mol % ( $C_{\text{fruc}} = 0.1$  M;  $C_{\text{acid}} = 1$  M; 140 °C) obtained at the highest acid concentration (1 M), lowest temperature (140 °C), and the lowest initial D-fructose concentration (0.1 M) in the range. For comparison, the experimental yield was 74 mol % at these conditions.

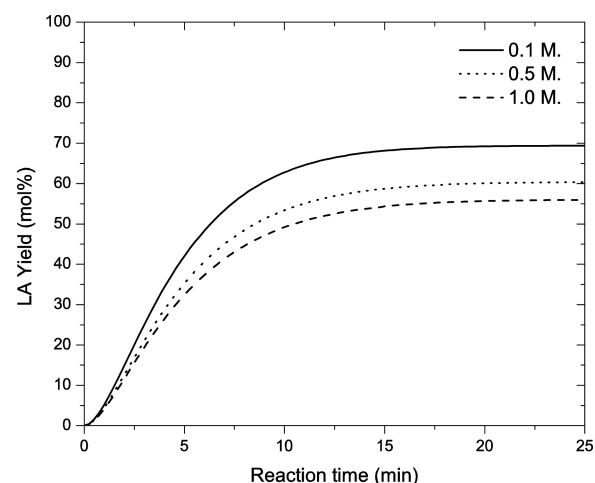
The modeled LA yield versus the batch time at different acid concentrations at a constant temperature (140 °C) and initial D-fructose concentration (0.5 M) is given in Figure 11. The highest yield was obtained with the highest acid concentration in the range (1 M). Another advantage of using a high acid concentration is higher reaction rates, as is clearly evident from



**Figure 11.** LA yield versus reaction time at different acid concentrations ( $T = 140$  °C,  $C_{\text{FRC},0} = 0.5$  M).

the profiles in Figure 11 (about 5 min to reach max LA yield at 1 M versus 1000 min at 0.01 M).

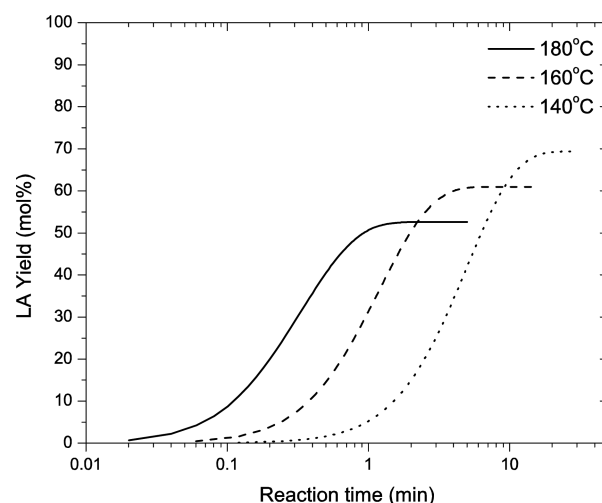
The maximum achievable LA yield is also a function of the initial D-fructose concentration, with lower concentrations giving higher LA yields (Figure 12). These findings may be explained by



**Figure 12.** LA yield versus reaction time at different initial D-fructose concentrations ( $T = 140$  °C, acid concentration = 0.5 M).

considering the orders in the desired reactions (D-fructose to HMF and HMF to LA) and the undesired humin formation reactions. The orders in D-fructose and HMF for the desired reactions are lower than for the humin forming reactions and as such the former are favored at lower concentration. Thus, higher LA yields are attainable at low D-fructose concentrations.

The LA yield versus the batchtime at three temperatures (140, 160, 180 °C) is given in Figure 13. The highest LA yield is



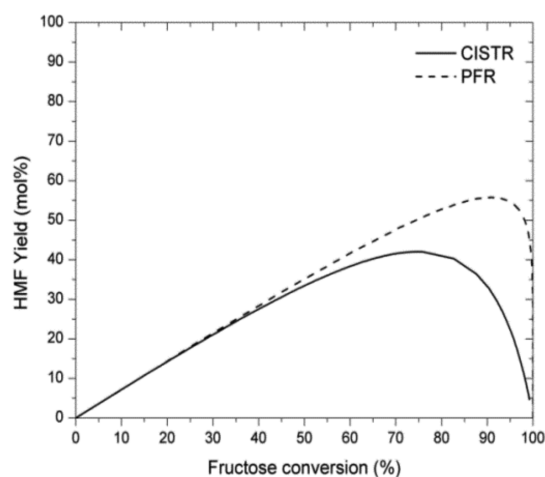
**Figure 13.** LA yield versus reaction time at different temperatures ( $C_{\text{FRC},0} = 0.1$ , acid concentration = 0.5 M).

attainable at the lowest temperature in the range. These findings may be rationalized by considering that the reaction of HMF to LA/FA has the lowest activation energy of all other reactions in the network (Tables 2 and 3) and as such will be favored at lower temperatures.

**Optimization of HMF and LA Yield in Stationary Continuous Reactor Configurations.** In continuous reactors, the yields of HMF and LA are a function of process parameters

( $T$ ,  $C_{\text{FRUC}}$ ,  $C_{\text{H}_2\text{SO}_4}$ , and residence time) as well as the extent of back mixing in the reactor. With the kinetic model available, the yield of HMF and LA in the two extremes regarding mixing, *viz* a PFR reactor and a continuously ideally stirred tank reactor (CISTR) were modeled. The calculation procedure is given in the Supporting Information.

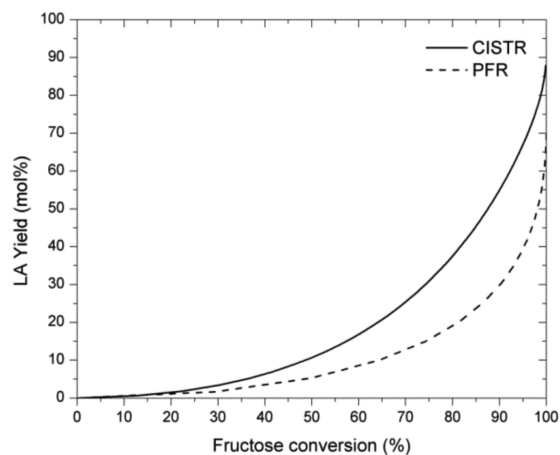
The HMF yield versus the D-fructose conversion at the highest temperature in the range (180 °C) for both reactor configurations is given in Figure 14.



**Figure 14.** HMF yield versus D-fructose conversion for a PFR and CISTR (180 °C, 0.1 M D-fructose feed, 0.005 M sulfuric acid).

As expected, the yield of HMF shows a clear maximum and the highest attainable yield (56%) is obtained in a PFR, whereas the yield is considerably lower in the CISTR (42%). Thus, a low extent of backmixing is favorable for a high HMF yield.

The LA yield versus the D-fructose conversion for the two reactor configurations at optimum conditions in the range to achieve high LA yields (140 °C, 1.0 M sulfuric acid, 0.1 M D-fructose, *vide supra*) is given in Figure 15. As anticipated based on the proposed reaction network, the yield increases with D-fructose conversion. Backmixing and thus the use of a CISTR is favored, in line with the observation that dilute D-fructose solutions are preferred to reduce humin formation. The yield of LA in a CISTR goes to a theoretical limit of 99+% in very dilute



**Figure 15.** LA yield versus D-fructose conversion for a PFR and CISTR (140 °C, 0.1 M D-fructose feed, 1.0 M sulfuric acid).

solutions, thus at high D-fructose conversion levels. However, it should be kept in mind that the reaction rate will reduce considerably at such highly dilute conditions. For instance, the model predicts a 99% LA yield in the CISTR after a residence time of 1250 years. Clearly, this leads to an unacceptable low STY, making these conditions unfavorable for commercial operation.

## CONCLUSIONS

A kinetic model for the acid-catalyzed reaction of D-fructose to HMF and LA in water with sulfuric acid at concentrations between 0.005 and 1 M, initial concentrations of D-fructose between 0.1 and 1 M, and a temperature window of 140–180 °C using the power-law approach has been developed. A maximum-likelihood approach has been applied to estimate the kinetic parameters for the main reaction to LA and FA and the side reactions to humins. A good fit between experimental data and the kinetic model was obtained.

The kinetic model implies that different strategies are required to obtain either a high HMF or LA yield. Highest yields for HMF (about 56 mol %) are attainable at a low acid concentration, whereas the temperature and the initial D-fructose concentration are of less importance. In addition, a reactor with a small extent of backmixing (PFR) is the preferred reactor configuration. For highest LA yields (74 mol %), a high acid concentration, low temperature, and low initial D-fructose concentration are favored and a CISTR is the most suitable configuration. The model proposed in this work will aid the rational design and operation of dedicated reactors for the conversions of various types of biomass feedstock to HMF and LA.

The results were compared with earlier kinetic studies in our group on the conversion of D-glucose to HMF/LA in water using sulfuric acid as the catalyst. D-Fructose is 2 orders of magnitude more reactive than D-glucose, and HMF yields are a factor of 10 higher. In addition, the LA yields for D-fructose are also substantially higher (about 10 mol %) than for D-glucose.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsschemeng.5b00023.

Figures with potential derivatives from HMF and LA, conversion versus time profiles for a number of representative runs and a parity plot with experimental and model data; tables with overviews of LA synthesis from D-fructose and the kinetic constants versus the temperature; detailed description of the kinetic modeling (PDF).

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### Notes

The authors declare no competing financial interest.

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