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Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural Using Sulfuric Acid in Water

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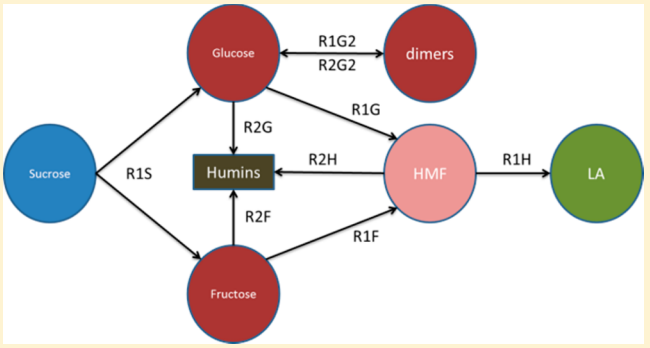
Supporting Information

ABSTRACT: We here report experimental and kinetic modeling studies on the conversion of sucrose to levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) in water using sulfuric acid as the catalyst. Both compounds are versatile building blocks for the synthesis of various biobased (bulk) chemicals. A total of 24 experiments were performed in a temperature window of 80−180 °C, a sulfuric acid concentration between 0.005 and 0.5 M, and an initial sucrose concentration between 0.05 and 0.5 M. Glucose, fructose, and HMF were detected as the intermediate products. The maximum LA yield was 61 mol %, obtained at 160 °C, an initial sucrose concentration of 0.05 M, and an acid concentration of 0.2 M. The maximum HMF yield (22 mol %) was found for an acid concentration of 0.05 M, an initial sucrose concentration of 0.05 M, and a temperature of 140 °C. The experimental data were modeled using a number of possible reaction networks. The best model was obtained when using a first order approach in substrates (except for the reversion of glucose) and agreement between experiment and model was satisfactorily. The implication of the model regarding batch optimization is also discussed.



1. INTRODUCTION

Levulinic acid (4-oxopentanoic acid, LA) is considered as a very important biobased platform chemical with a wide derivatization and application range.[1−9] It is accessible by the acid catalyzed hydrolysis of the C6-sugars in various biomass sources.[1−4,10−18] Typical byproducts are formic acid and humins. The latter are oligomeric/polymeric substances that are either soluble or insoluble in the reaction mixture. HMF, also a very versatile platform chemical, is an intermediate in the conversion of C6 sugars to LA. HMF yields are a strong function of the C6 sugar used and best results have been reported with ketohexoses like fructose and psicose.[19] The yields from aldohexoses such as glucose are by far lower and typically below 10 mol %.

The Biofine Company has been actively involved in the conversion of lignocellulosic biomass to LA in the last 15 years.[20] In their process, the lignocellulosic biomass and sulfuric acid catalyst are mixed in water, and the resulting slurry is supplied to the reactor section. The reaction conditions, typically 180−210 °C, are such that formic acid and furfural, the two major low molecular weight byproducts, are vaporized and collected separately. The liquid phase with the LA and solids (humins, lignins) is filtered to obtain an aqueous LA solution, which is neutralized and further purified to obtain LA. Typical yields of LA are between 15 and 41 wt % on feed, the exact value being a function of the reaction conditions and biomass source. GFBiochemicals recently reported a Biofine derived process to produce LA from a wide range of biomass feeds. Yield improvements were reported based on further optimization/modification of the reactor and workup section, though details are to the best of our knowledge not reported yet. Commercial production in Casserta, Italy, started in the summer of 2015. The unit will be scaled up to a full capacity of 10 000 MT/a by 2017.[21]

A wide range of biomass feeds has been reported for LA synthesis, including both monomeric and dimeric sugars as well as complex biomass sources such as Mischantus,[22] starch,[23] wood cellulose[24,25] and waterhyacynth.[26] Among them, sucrose has also been studied.[1−3,18,27−32] It is easily hydrolyzable to its

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Table 1. Selected Examples for LA and HMF Synthesis from Sucrose in Water Using Homogeneous Brönsted Acid Catalysts

no.	sucrose concn	cat.	cat. concn	time	T (°C)	P (atm)	HMF yield[a] (mol %)	LA yield[a] (mol %)	ref
1	0.66 M	H_2SO_4	1.80 M	8 h	140		n.d.	40−50[b]	32
2	0.05 M	H_2SO_4	0.001 M	32 s	250	341	25	n.d.	34
3	0.18 M	H_2SO_4	1 M	16 h	125		n.d.	42[b]	28
4	1.17 M	HCl	2 M	24 h	100		n.d.	21−22	27
5	0.86 M	HCl	2 M	1 h	162	7	n.d.	42−43	18
6	0.18 M	HCl	3 M	16 h	125		n.d.	60[b]	28
7	0.29 M	HCl	6 M	5 h	108		n.d.	62	29
8	0.33 M	HCl	3.84 M	1 h	98		n.d.	50[b]	31
9	0.18 M	HBr	1 M	16 h	125		n.d.	70[b]	28
10	25 wt %	oxalic acid	0.03 M	2.5 h	145, 15 min then 125		27	n.d.	35
11	23 wt %	oxalic acid	0.23 wt %	3 h	200	3	25	n.d.	36

[a]Yields are based on monosaccharide concentration. [b]Not clear whether yields are based on mol % or wt %, or on monosaccharide or sucrose concentration.

monomers, D-glucose and D-fructose, which both can be converted to LA in good yields. Sucrose is present in high amounts in sugar cane and sugar beets. Waste streams of the sugar industry contain significant amounts of sucrose and this justifies a detailed study on the use of sucrose for LA synthesis.

The first studies on the conversion of sucrose to LA were reported in 1873 by Grote and Tollens.[10] Later studies reported the use of various mineral acids such as hydrochloric acid, sulfuric acid, and hydrobromic acid as well as heterogeneous catalysts.[18,27,28,30,31,33] Table 1 summarizes a number of representative studies on the acid-catalyzed conversion of sucrose to HMF and LA using homogeneous Brönsted acid catalysts. The highest reported LA yield is about 70 mol %, whereas the maximum HMF yield is limited to about 27%.

Kinetic studies on the conversion of sucrose to HMF/LA using simple homogeneous Brönsted acids such as sulfuric acid in water have to the best of our knowledge not been reported in the literature. Recently, Woodley et al. published a kinetic study on the conversion of glucose−fructose mixtures using HCl as the catalyst in an acetone−water mixture.[37] Kinetic studies are of prime importance for a proper design of the reactor section of LA processes and also allow selection of the best operating conditions to achieve maximum yields and volumetric production rates of LA.

In this paper, the kinetics of the conversion of sucrose to LA using a batch setup is studied in a broad range of process conditions (80−180 °C, sulfuric acid concentrations between 0.005−0.50 M, and initial sucrose concentrations between 0.05−0.50 M). The concentrations of the intermediates (glucose, fructose, and HMF) were also determined, and these components were included in the kinetic analysis. On the basis of the experimental data, a reaction network is proposed and the experimental data were modeled using a kinetic scheme in line with this proposal. Furthermore, a number of alternative kinetic networks were evaluated, and the results are compared with the original scheme. Finally, the optimum conditions for batch processing to obtain the highest LA/HMF yields were determined on the basis of the model and will be discussed.

2. METHODS AND ANALYSIS

2.1. Chemicals. All chemicals were of analytical grade and were used without further purification. Concentrated sulfuric acid (95−97 wt % [CASRN 7664-93-9]) and formic acid (98−100 wt % [CASRN 64-18-6]) were purchased from Merck KGaA (Darmstadt, Germany). Sucrose (≥95 wt % [CASRN 57-50-1]) and fructose (≥95 wt % [CASRN 57-48-7]) were acquired from Fisher Scientific UK (Leicestershire, Great Britain); glucose (≥99.5 wt % [CASRN 14431-43-7]), 5-hydroxymethylfurfural (≥99 wt % [CASRN 67-47-0]) and levulinic acid (98 wt % [CASRN 123-76-2]) were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Deionized water was used to prepare the various solutions.

2.2. Experimental Procedures. All reactions were carried out in glass ampules with an internal diameter of 3 mm, a wall thickness of 1.5 mm, and a length of 15 cm. These were filled at room temperature with a solution of sucrose and sulfuric acid (total liquid volume of 0.5 cm^3) and then sealed with a torch. A series of ampules was placed in a rack and placed in a constant temperature oven (±1 °C) which was preset at the desired reaction temperature. At different reaction times, an ampule was taken from the oven and directly quenched into a cold water bath. The liquid content was then filtered using a PTFE syringe filter (0.45 μm, VWR, The Netherlands). The particle free aliquot was then diluted 7−8 times with water prior to HPLC analysis.

2.3. Analytical Methods. The composition of the liquid phase was determined using two different HPLC systems. An Agilent 1200 HPLC consisting of a Hewlett-Packard 1200 pump and a Bio-Rad organic acid column (Aminex HPX-87H) was used for glucose, fructose, HMF, and LA analysis. A typical example of a chromatogram is given in Figure S1 (Supporting Information). For glucose, fructose, and LA, quantification was performed using an RID detector, whereas a UV detector was used for HMF. An aqueous sulfuric acid (5 mM) solution was used as the mobile phase at a flow rate of 0.55 cm^3 per minute. The column was operated at 60 °C. The analysis of a sample was complete within 60 min.

An Agilent 1050 HPLC consisting of a Hewlett-Packard 1050 pump, a Bio-Rad sugar column (Aminex HPX-87P), and a Waters 410 refractive index detector was used for sucrose quantification. Double distilled water was used as the mobile phase at a flow rate of 0.55 cm^3 per minute. The column was operated at 80 °C. The analysis of a sample was complete within 30 min.

The concentrations of each compound in the product mixture were determined using calibration curves obtained by analyzing standard solutions of known concentrations.

2.4. Definitions. The conversion of sucrose (X_{SUC}) and the yields of HMF (Y_{HMF}) and LA (Y_{LA}) are defined in eq 1−3.

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

$$Y_{HMF} = \frac{(C_{HMF})}{2C_{SUC,0}} \quad (2)$$

$$Y_{LA} = \frac{(C_{LA})}{2C_{SUC,0}} \quad (3)$$

Here, $C_{SUC,0}$ is the initial concentration of sucrose. All definitions are on a molar basis.

2.5. Determination of the Kinetic Parameters. The kinetic parameters were determined using a nonlinear least-squares approach using the MATLAB function *lsqnonlin*, which is based on an Trust-Region-Reflective algorithm, and involves minimization of the errors between the experimental data and the kinetic model. Details about this procedure can be found in the literature.[38,39]

3. RESULTS AND DISCUSSION

3.1. Experimental Studies. A total of 24 experiments were performed in a temperature window of 80−180 °C, a sulfuric acid concentration between 0.005 and 0.5 M, and an initial sucrose concentration between 0.05 and 0.5 M. Main products (HPLC) are fructose, glucose, HMF, LA, and formic acid (FA), in line with earlier studies.[1−3,8,32] The latter was not quantified in detail. Upon reaction, the color of the reaction mixtures changed from transparent to yellowish-brown, and in some cases solid dark brown byproducts (humins) were formed. These are formed by condensation reactions of products and intermediates, and were not quantified. In addition, soluble humins may be formed as well.

The concentrations of the main products as a function of the batch time were determined (HPLC), and the results for two representative experiments are given in Figures 1 (120 °C) and 2 (180 °C).

The conversion rate of sucrose is a strong function of temperature and acid concentration. The time for quantitative conversion is typically less than 1 min at temperatures exceeding 120 °C, and as such sucrose is not observed in most reaction mixtures (Figure 2). At low temperatures (80 and 100 °C) and low acid concentrations, sucrose is detected in the reaction mixtures for up to 20 min (100 °C, 0.005 M H_2SO_4). As expected, glucose and fructose are the initial products and are derived from the acid catalyzed hydrolysis (inversion) of sucrose. The glucose and fructose yields are around 100%, indicating that sucrose inversion is very selective in the experimental window of process conditions.

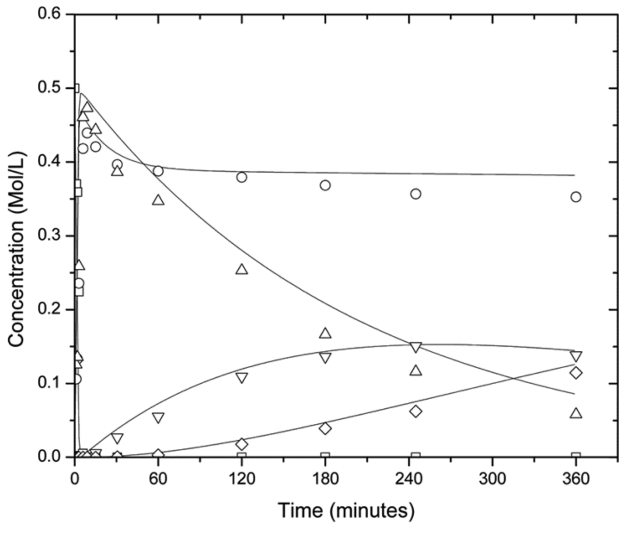

Figure 1. Typical time−concentration profile of the products of the acid-catalyzed hydrolysis of sucrose at 120 °C, $C_{H_2SO_4}$ = 0.05 M, $C_{SUC,0}$ = 0.5 M. Symbols denote experimental values: (□) sucrose, (○) glucose, (△) fructose, (▽) HMF, (◇) LA. Lines, model.

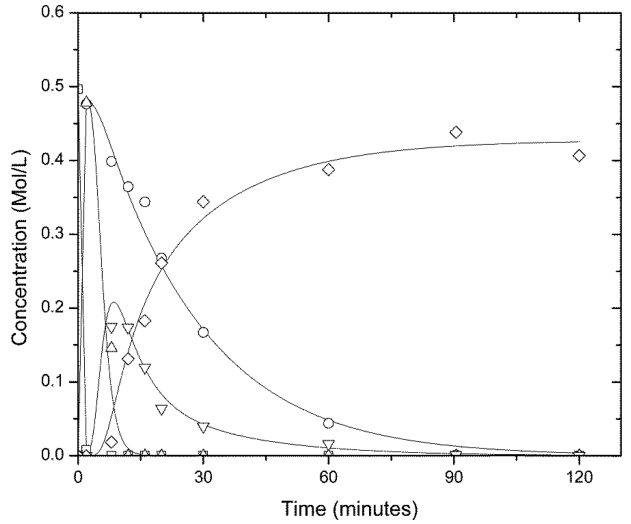

Figure 2. Typical time−concentration profile of the products of the acid-catalyzed hydrolysis of sucrose at 180 °C, $C_{H_2SO_4}$ = 0.05 M, $C_{SUC,0}$ = 0.5. Symbols denote experimental values: (□) sucrose, (○) glucose, (△) fructose, (▽) HMF, (◇) LA. Lines, model.

Glucose, fructose, and HMF are typical intermediates and in some cases (particularly at higher severity) show a clear maximum, whereas LA is formed in significant amounts upon prolonged batch times. Glucose is by far less reactive than fructose. These findings are in line with earlier kinetic studies from our group on the conversion of the individual sugars (Figure 3).[40] Here, it was demonstrated that on average, fructose is about 100 times more reactive than glucose in the temperature window employed in this study.

LA is stable under the experimental conditions employed as is evident from a constant concentration level at prolonged reaction times (up to 900 min, data not shown for brevity). The maximum experimental LA yield was 61 mol %, obtained at 160 °C, an initial sucrose concentration of 0.05 M and an acid concentration of 0.2 M. The maximum LA yield in this study is higher than reported in the literature for sucrose when using sulfuric acid as the catalyst (40−50 mol %).[32] It is also of interest to compare the experimental LA yields with previous studies using the individual sugars (glucose, fructose) in water with sulfuric acid as the catalyst. For fructose alone, the highest experimental yield was 74 mol % (fructose concentration of 0.1 M, a sulfuric acid concentration of 1 M, and a temperature of 140 °C),[40] whereas the best yields for glucose were somewhat lower (60%, 140 °C; $C_{GLC,0}$, 0.1 M; C_{acid}: 1 M).[8] Though the experimental conditions are different, the data imply that the experimentally observed highest LA yield for sucrose in this study is in line with the values obtained for experiments with the individual sugars.

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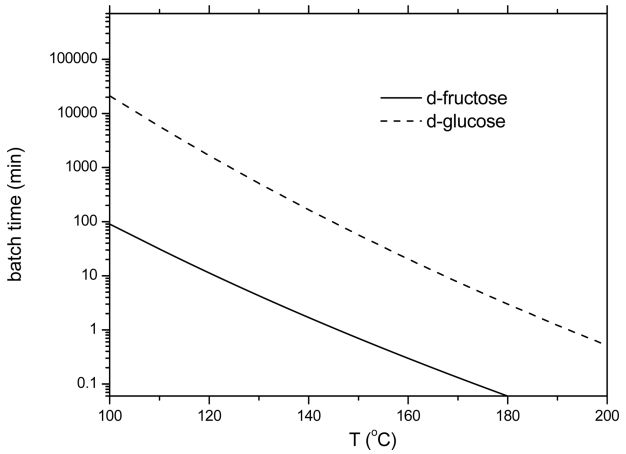

Figure 3. Required batch time for 90% C6-sugar conversion (fructose and glucose) versus temperature in water using sulfuric acid as the catalyst (1 M). Reproduced from ref 40. Copyright 2015, American Chemical Society.

The maximum HMF yield within the experimental window of process conditions was 22 mol % (0.05 M sulfuric acid, 0.05 M sucrose, 140 °C). This value is slightly lower than reported in the literature for sucrose in water using sulfuric acid as the catalyst (25 mol %, see Table 1), though comparison is hampered as the experimental conditions are different. For fructose alone, the highest reported HMF yield in water using sulfuric acid is 53 mol % (initial fructose concentration of 0.1 M, a sulfuric acid concentration of 0.01 M and a temperature of 180 °C).[40] For glucose, the HMF yield is considerably lower and for instance Girisuta et al. reported a maximum yield of 5 mol % in water using sulfuric acid as the catalyst in a similar window of process conditions.[8] As such, the value of 22 mol % for sucrose is in line with the literature, particularly when considering that the initial inversion of sucrose to fructose and glucose is fast and essentially quantitative.

Glucose can be isomerized to fructose, though the reaction is known to be slow in the absence of catalysts and equilibrium limited in water. At 150 °C, the equilibrium constant in water is about 1.[41] In this study, the rate of glucose−fructose isomerization appears to be slow compared to the time scale of the other reactions, particularly at low temperatures. This is illustrated by Figure 1, showing that the glucose concentration is about constant after its initial formation from sucrose, whereas the fructose concentration is dropping more rapidly. In case of the occurrence of a rapid isomerization reaction, a different profile is expected with a constant fructose-to-glucose ratio.

Of interest is the observation of a small drop in the glucose concentration directly after its formation from sucrose, see Figure 1 for a representative example. This effect is particularly evident for experiments carried out in the lower temperature range. A possible explanation is the formation of reversion products of glucose, mostly dimers, as also proposed by Johnson et al.[42] These reactions are known to be relatively fast and equilibrium limited (*vide infra*). For fructose, this trend is not observed, likely due to the fact that fructose is by far more reactive than glucose and already converted to a significant extent directly after its formation.

3.2. Kinetic Modeling Studies. *3.2.1. Reaction Network Development.* The experimental data were initially modeled (model 1) with a global reaction network given in Figure 4. The reaction network is based on earlier reaction networks proposed for experimental and kinetic modeling studies for glucose and fructose individually.[8,40] The latter is justified as it was shown experimentally that sucrose is rapidly hydrolyzed and inverted to a 1 to 1 molar mixture of fructose and glucose.

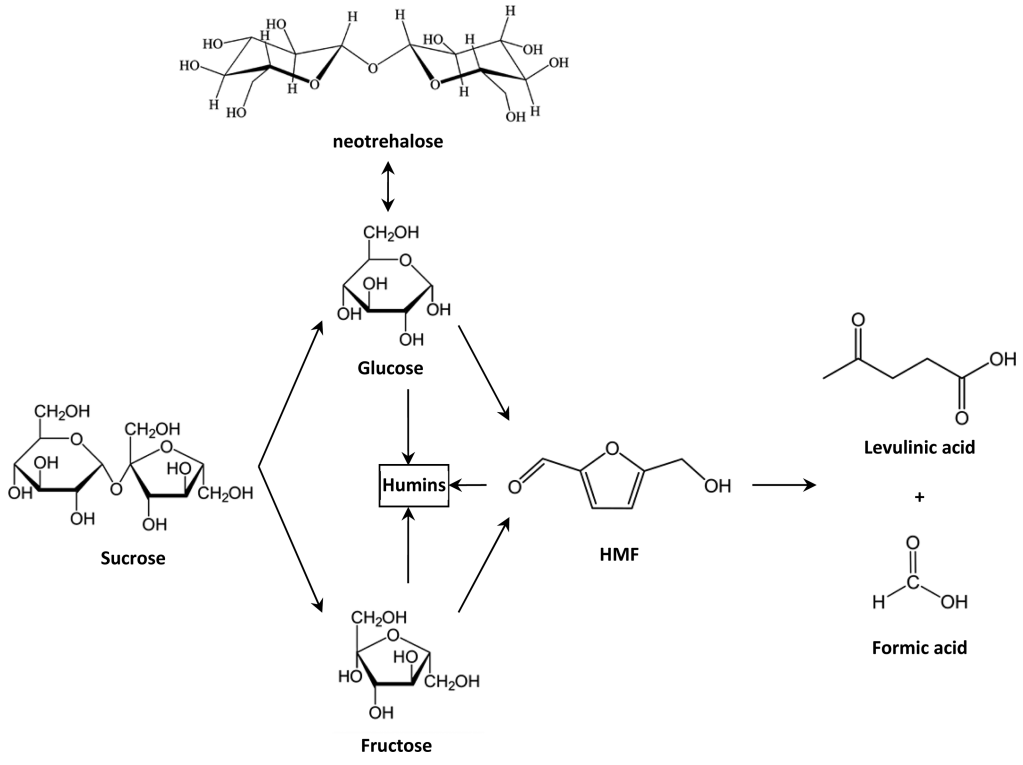

Figure 4. Proposed reaction network (model 1) for the conversion of sucrose to LA and HMF.

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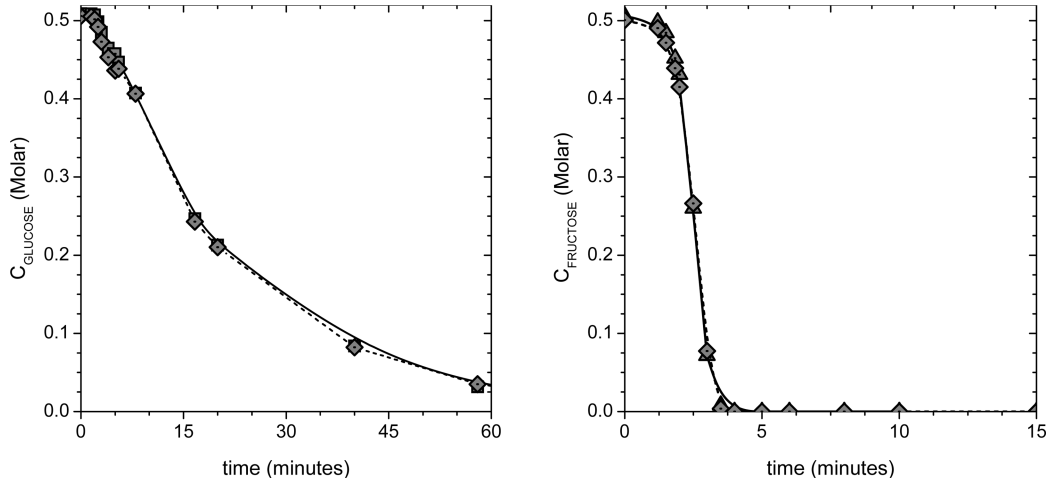

Figure 5. Concentration−time profiles for glucose and a mixture of glucose and fructose (1 to 1 molar ratio, left) and fructose and a mixture of fructose and glucose (1 to 1 molar ratio, right). $C_{GLU,0} = C_{FRU,0} = 0.50$ M, 180 °C, $C_{H_2SO_4} = 0.05$ M.

Table 2. Overview of Kinetic Studies on Sucrose Hydrolysis to Glucose and Fructose

no.	$C_{SUC,0}$ [M]	C_{acid} [M]	conditions	T [°C]	t [h]	R_{SUC}/mol L^{-1} min^{-1}[a]	ref
1	0−2.63	$C_{H^+} = 3 \times 10^{-7}$ − 0.1	isothermal operation	20−130	n.a.	$R_{SUC} = 2.8 \times 10^{16} \exp\left[-\frac{108\,570}{RT}\right] C_H{}^+ C_{SUC}$	44
2	0.01−0.1	$C_{H_2SO_4} = 0.10$−1.0	isothermal operation	45−55	0.50	$R_{SUC} = 2.8 \times 10^{15} \exp\left[\frac{-99\,160}{RT}\right] C_H{}^+ C_{SUC}$	45
3	0.07	$C_{H_2SO_4} = 0.01$−0.20	isothermal operation	160−200	0.05−0.20	too fast, not observable	46
4	0.06	$C_{HCl} = 5 \times 10^{-4}$	nonisothermal, linear gradient	70−98	15	$R_{SUC} = 3.5 \times 10^{12} \exp\left[\frac{-102\,330}{RT}\right] C_H{}^+ C_{SUC}$	
				60−98	16	$R_{SUC} = 1.7 \times 10^{13} \exp\left[\frac{-105\,970}{RT}\right] C_H{}^+ C_{SUC}$	47
				60−90	15	$R_{SUC} = 7.8 \times 10^{12} \exp\left[\frac{-103\,720}{RT}\right] C_H{}^+ C_{SUC}$	
5	0.03	$C_{HCl} = 0.25$	continuous flow nonisothermal, ramp time of 2.5 s, flow rate of 450 mL/min	T_{set} = 151 (151−155)	0.0125	$R_{SUC} = 1.4 \times 10^{14} \exp\left[\frac{-112\,700}{RT}\right] C_H{}^+ C_{SUC}$	48
				T_{set} = 144 (144−150)	0.0125	$R_{SUC} = 7.2 \times 10^{14} \exp\left[\frac{-117\,700}{RT}\right] C_H{}^+ C_{SUC}$	
				T_{set} = 139 (139−146)	0.0125	$R_{SUC} = 4.2 \times 10^{12} \exp\left[\frac{-100\,200}{RT}\right] C_H{}^+ C_{SUC}$	49
6	0.015, 0.15, 0.73	$C_{HCl} = 10^{-4}$−10^{-8}	pressure of 10 MPa, subcritical water	160−200	1−4 min	$R_{SUC} = 3.8 \times 10^{11} \exp\left[\frac{-98\,000}{RT}\right] C_H{}^+ C_{SUC}$	
7	3×10^{-3}	$C_{HNO_3} = 0.5$−2.5	nonisothermal method	50−90	0.83	$R_{SUC} = 2.9 \times 10^{15} \exp\left[\frac{-99\,000}{RT}\right] C_H{}^+ C_{SUC}$	50
8	0.26	$C_{H^+} = 0.34$ (>1.70 Na^+ eq/L, 800 g/L)	microwave, Amberlite 200 °C	40−80	500	$R_{SUC} = 3.8 \times 10^{12} \exp\left[\frac{-92\,800}{RT}\right] C_H{}^+ C_{SUC}$	51

[a] T in K.

In acidic media, glucose may dehydrate inter- and intramolecularly to form glucose oligomers and anhydroglucoses (mainly levoglucosan, LG), respectively.[42] Literature studies revealed that up to 12 wt % of the glucose is converted into reversion products at high sugar loadings (200 mg·cm^{-3}). The reversion products are mainly disaccharides, and larger oligosaccharides were not reported to be formed in significant amounts. In Figure 4, only one (neotrehalose) of the possible reversion dimers is shown. Disaccharide formation was modeled using a second-order dependency in glucose. In addition, the dimerization reaction is known to be reversible and this was also assumed in our model. Johnson et al.[42] also reported the formation of levoglucosan (LG) from glucose, though only in significant amounts at low glucose concentrations (<10 mg·cm^{-3}). LG was also not detected in this study, and as such this reversion product was not included in the kinetic models.

The equilibrium reaction between glucose and fructose was also not included in the first model. This reaction is known to be catalyzed by (inorganic) bases and enzymes. Acids are known to be less effective and the acid catalyzed isomerization reaction is known to be by far slower than the base-catalyzed

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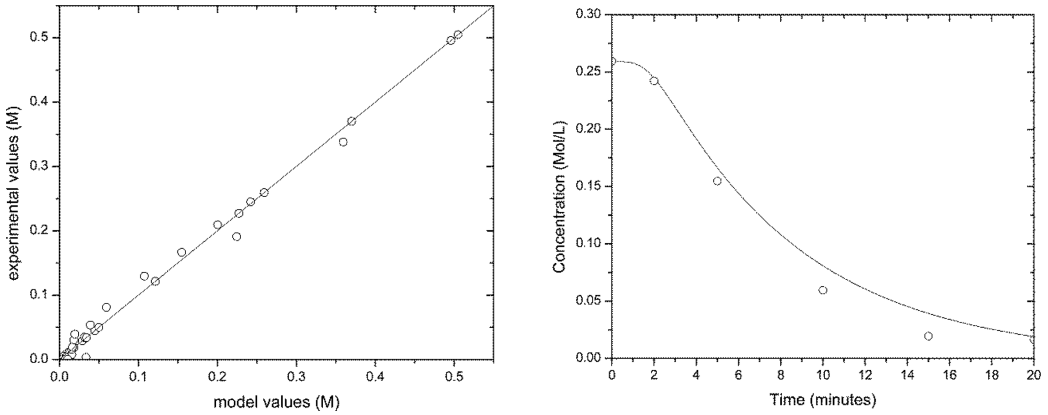

Figure 6. Parity plot for experimental and model data (left) and a representative concentration−time curve (right) for the reaction of sucrose to glucose and fructose. Conditions (right), T = 100 °C, $C_{SUC(0)}$ = 0.26 M, C_{acid} = 0.005 M.

isomerization. For instance, Watanabe et al. showed that fructose reacts in acidic aqueous media to HMF with negligible glucose formation.[43] However, when starting with glucose, some fructose besides HMF and LA were observed. As such, glucose−fructose isomerization was included in subsequent kinetic models (*vide infra*).

Furthermore, model 1 assumes that both fructose and glucose react independently to HMF. This assumption is based on literature evidence for kinetic studies using glucose[8] only and recent studies by Woodley et al. for fructose−glucose mixtures in water−acetone as the solvent.[37] In the latter, the reaction of glucose to HMF was required to obtain a better model description of the experimental data.

Finally, it is assumed that glucose, fructose, and HMF individually react to soluble and insoluble humins, as proposed for studies with the individual sugars. This is a simplification as cross condensations between the various intermediates (fructose, glucose, HMF) cannot be excluded beforehand. The possibility of cross condensations between glucose and fructose to form humins was investigated independently. For this purpose, the concentration−time profile for the individual sugar was compared to that of a mixture of both sugars in a 1 to 1 ratio. The results for two representative experiments are given in Figure 5. It shows that the concentration−time profiles for the individual sugars are not affected in the presence of the other sugar, implying that cross condensation reactions between the two sugars do not take place to a considerable extent.

3.2.2. Model Development. The first kinetic model (model 1) was developed based on the reaction network given in Figure 4 and assumes first-order reactions in most substrates. As the reaction rate of sucrose inversion to glucose and fructose is much faster than for the consecutive reactions, the inversion of sucrose was modeled independently. In a later stage, extended reaction networks (including glucose−fructose isomerization) were modeled and the results will be provided in a separate paragraph.

3.2.3. Kinetic Modeling of Sucrose Conversion to Glucose and Fructose. The kinetic model for the conversion of sucrose to glucose and fructose was developed using eight experiments from the data set with a total of 29 data points. Only this limited data set could be used as sucrose is converted on the time scale of less than a minute at the higher temperatures within the temperature window.

The inversion of sucrose to fructose and glucose is typically modeled in the literature using a first order approach in acid and sucrose (Table 2) and a similar approach was used in this study.

For a batch reactor, the mass balance for sucrose is given in eq 4.

$$\frac{dC_{SUC}}{dt} = -R_{1S} \tag{4}$$

When assuming first order reactions, R_{1S} is given by eq 5.

$$R_{1S} = k_{1S}(C_{SUC})(C_{H^+}) \tag{5}$$

The temperature dependence of the kinetic constant was considered using a modified Arrhenius equation as given in eq 6.

$$k_{1S} = k_{1RS}\ \exp^{[Ea_{1S}/R((T-T_R)/T_RT)]} \tag{6}$$

where T_R is the reference temperature (140 °C), k_{1RS} is the rate constant at reference temperature and E_{a1S} is the activation energy.

At the start-up of the reaction, the reaction takes place nonisothermally due to heating-up of the contents of the ampule from room temperature to the oven temperature. The experimental profiles at different temperatures were modeled using a heat balance for the contents in an ampule using eq 7 and 8.

$$\frac{d(MCpT)}{dt} = UA_t(T_{oven} - T) \tag{7}$$

$$T = T_{oven} - (T_{oven} - T_i)\ \exp^{-ht} \tag{8}$$

The value of h was shown to be a function of the set-point of the oven. This temperature dependence was determined by fitting the calculated h-values at different set points of the oven (80−180 °C) and was found to be described properly using a simple linear relation (eq 9):

$$h(T) = 0.00128.T(\mathrm{K}) \tag{9}$$

The actual H^+ concentration was calculated using eq 10.

$$C_{H^+} = C_{H_2SO_4} + \frac{1}{2}(-K_{a,HSO_4^-} - C_{H_2SO_4} + \sqrt{(K_{a,HSO_4^-} + C_{H_2SO_4})^2 + 4C_{H_2SO_4}K_{a,HSO_4^-}}) \tag{10}$$

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Here K_{a,HSO_4^-} represents the dissociation constant of HSO_4^-. The temperature dependence of this dissociation constant is given in eq 11 (T in K).[52]

$$pKa_{HSO_4^-} = 0.0152.T - 2.636 \quad (11)$$

The kinetic constants and the activation energies were determined using the MATLAB software package by simultaneous modeling of the 8 selected experiments. Good agreement between model and experimental data was obtained, as is evident from a parity plot and the time concentration graph of a selected experiment (Figure 6). The estimated value for k_{1RS} was 730 ± 290 L mol^{-1} min^{-1} and 110 ± 10 kJ mol^{-1} for the activation energy. The experimentally determined activation energy for the reaction is within the 93−118 kJ mol^{-1} range as reported in the literature (Table 2).

3.2.4. Kinetic Modeling Using Network 1. A simplified representation of the reaction network of model 1 (Figure 4) including a labeling scheme of the individual reactions is given in Figure 7. For all reactions a first order approach in reactants

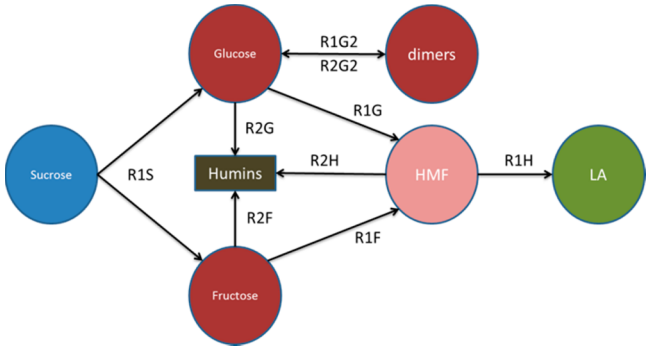

Figure 7. Schematic representation of the reaction network for kinetic model 1.

was applied, the only exception being the reaction of glucose to glucose dimers, which was assumed to be second order. The kinetic constants for sucrose inversion to fructose and glucose were fixed to the model values obtained in the previous paragraph.

The individual reaction rates are defined in eq 12−19.

$$R_{1F} = k_{1F}(C_{FRC})(C_{H^+}) \quad (12)$$

$$R_{2F} = k_{2F}(C_{FRC})(C_{H^+}) \quad (13)$$

$$R_{1G} = k_{1G}(C_{GLC})(C_{H^+}) \quad (14)$$

$$R_{2G} = k_{2G}(C_{GLC})(C_{H^+}) \quad (15)$$

$$R_{1H} = k_{1H}(C_{HMF})(C_{H^+}) \quad (16)$$

$$R_{2H} = k_{2H}(C_{HMF})(C_{H^+}) \quad (17)$$

$$R_{1G2} = k_{1G2}(C_{GLC})^2(C_{H^+}) \quad (18)$$

$$R_{2G2} = k_{2G2}(C_{G2})(C_{H^+}) \quad (19)$$

The temperature dependencies of the kinetic rate constants were defined in term of modified Arrhenius equation like the one given in eq 6, and a reference temperature of 140 °C was used.

For a batch reactor setup, the concentrations of the individual species are a function of time. When using the proposed kinetic model as given in Figure 7, these are represented by the following differential equations:

$$\frac{dC_{FRC}}{dt} = R_{1S} - R_{1F} - R_{2F} \quad (20)$$

$$\frac{dC_{GLC}}{dt} = R_{1S} - R_{1G} - R_{2G} - R_{1G2} + 2R_{2G2} \quad (21)$$

$$\frac{dC_{HMF}}{dt} = R_{1F} + R_{1G} - R_{1H} - R_{2H} \quad (22)$$

$$\frac{dC_{LA}}{dt} = R_{1H} \quad (23)$$

$$\frac{dC_{G2}}{dt} = \frac{1}{2}R_{1G2} - R_{2G2} \quad (24)$$

3.2.5. Modeling Results for Model 1. A total of 24 experiments with 884 experimental data points, being the concentrations of glucose, fructose, HMF, and LA at different reaction times, was used for the development of the kinetic model. The best estimation of the kinetic parameters and their standard deviations were determined using a MATLAB optimization routine and the results are given in Table 3.

Table 3. Model Results for Model 1 (Figure 7)

k value at 140 °C	model result	±	dimension
k_{1G}	0.009	0.002	L mol^{-1} min^{-1}
k_{2G}	0.005	0.002	L mol^{-1} min^{-1}
k_{1F}	0.361	0.016	L mol^{-1} min^{-1}
k_{2F}	0.200	0.020	L mol^{-1} min^{-1}
k_{1HMF}	0.225	0.010	L mol^{-1} min^{-1}
k_{2HMF}	0.026	0.019	L mol^{-1} min^{-1}
k_{1G2}	0.227	0.057	L^2 mol^{-2} min^{-1}
k_{2G2}	1.427	0.394	L mol^{-1} min^{-1}
Ea_{1G}	153	14	kJ mol^{-1}
Ea_{2G}	172	19	kJ mol^{-1}
Ea_{1F}	116	3	kJ mol^{-1}
Ea_{2F}	122	5	kJ mol^{-1}
Ea_{1HMF}	92	3	kJ mol^{-1}
Ea_{2HMF}	146	43	kJ mol^{-1}
Ea_{1G2}	55	14	kJ mol^{-1}
Ea_{2G2}	99	17	kJ mol^{-1}

Agreement between model 1 and experiment is good, as illustrated by the overall parity plot, the parity plot for LA (Figure 8), and a number of modeled profiles in Figure 9.

Inspection of the kinetic constants at reference temperature in Table 3 show that the sucrose inversion to fructose and glucose is by far the fastest reaction in the network followed by the glucose dimerization equilibrium reaction, which is in line with the experimental findings (Figure 1). In addition, the kinetic constant for the reaction of glucose to HMF is about 40 times lower than for the reaction of fructose to HMF, which is also in agreement with studies for the individual sugars.[40]

It is of interest to compare the activation energies for the main reactions with those provided in the literature for aqueous systems using homogeneous catalysts (glucose[43,53−57] and fructose to HMF[40,58−60] and HMF to LA[40,53−56,58,60−63]). The results are provided in Figure 10 and Figure 11.

The activation energy for glucose to HMF found in this study (153 ± 14 kJ mol^{-1}) is equal within the confidence

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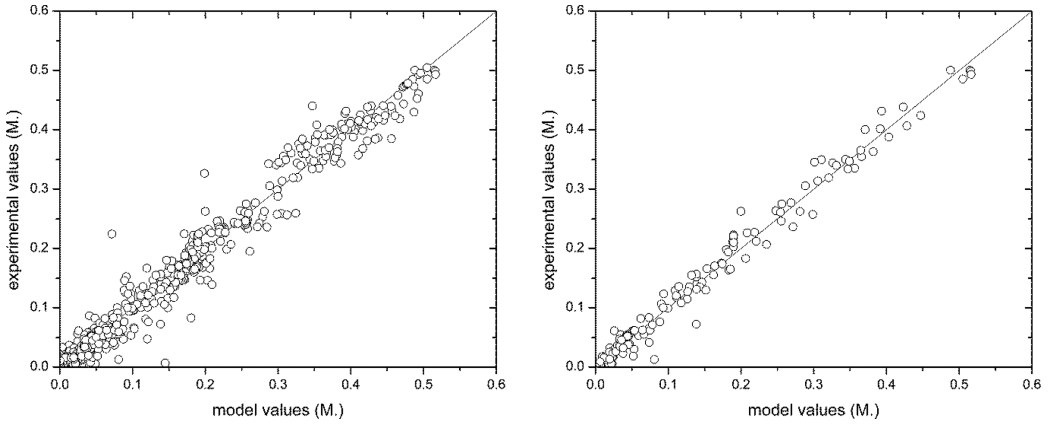

Figure 8. Parity plot for model 1 including the concentrations of all components (left) and only LA (right).

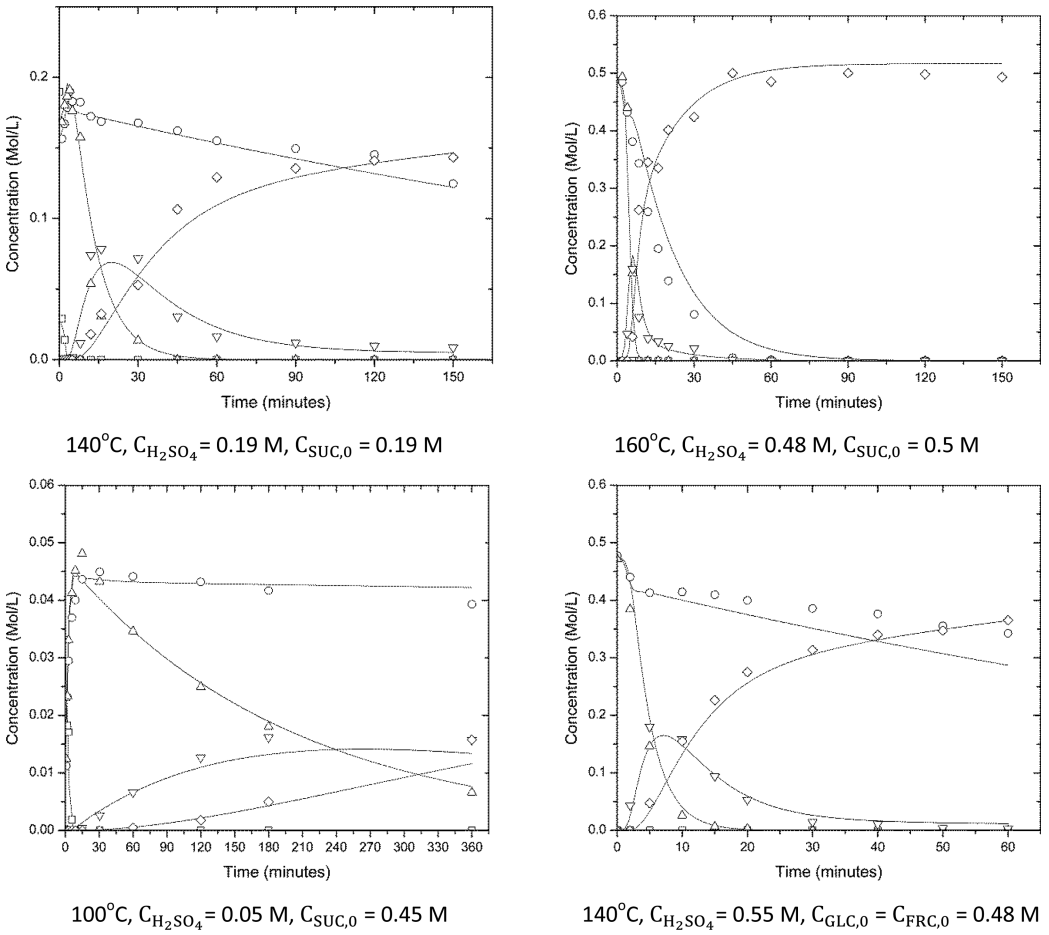

Figure 9. Experimental data points and model lines (model 1) for a number of representative batch experiments. Symbols denote experimental values: (□) sucrose, (○) glucose, (△) fructose, (▽) HMF, (◇) LA. Lines, model 1.

interval to the value reported for the reaction using the individual sugar as the starting material (152 ± 1 kJ mol^{-1}) and sulfuric acid as the catalyst by Girisuta et al.[8] For fructose, a broad range of activation energies has been reported (Figure 10, right). The value of 116 ± 3 kJ mol^{-1} is close to that reported for fructose-only studies (123 ± 5 kJ mol^{-1}) using sulfuric acid as the catalyst by Fachri et al.[40] The activation energies reported in the literature for the conversion of HMF to LA show a large spread (Figure 11). However, the value found here (92 ± 3 kJ mol^{-1}) is within the range and close to those found previously for kinetic modeling studies in our group for fructose and glucose only (111 ± 1 and 92 ± 5 kJ mol^{-1})[8,40] using sulfuric acid as the catalyst.

In the reaction network of model 1, all intermediates (glucose, fructose, and HMF) may either react to desired products or to humins. The activation energies for the desired reactions are all lower than for those forming humins (Table 3). This suggests that LA formation will be favored when the reaction is carried out at lower temperatures (*vide infra*).

3.2.6. Alternative Kinetic Models. A number of kinetic models derived from alternative reaction networks were explored and the results were compared with those for model

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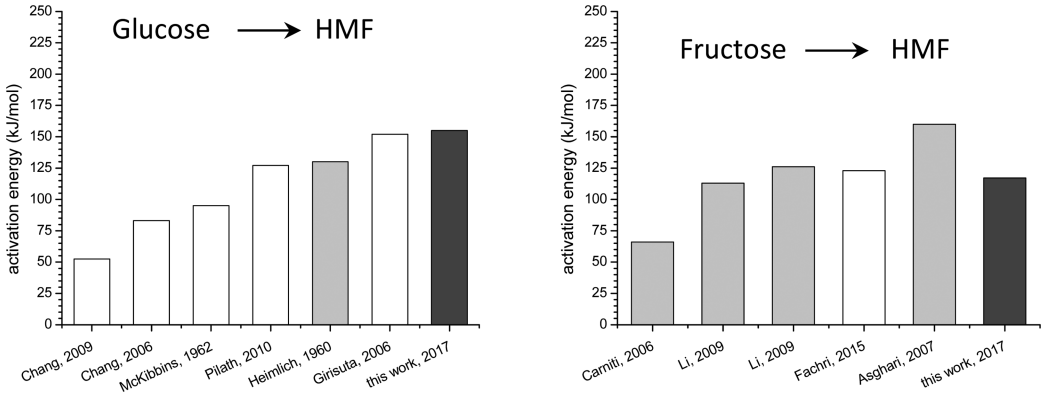


Figure 10. Overview of activation energies for the Brönsted acid catalyzed conversion of glucose (left) and fructose (right) to HMF in water: (white bars) using sulfuric acid catalys; (gray bars) other acid catalysts; (black bar) this study.

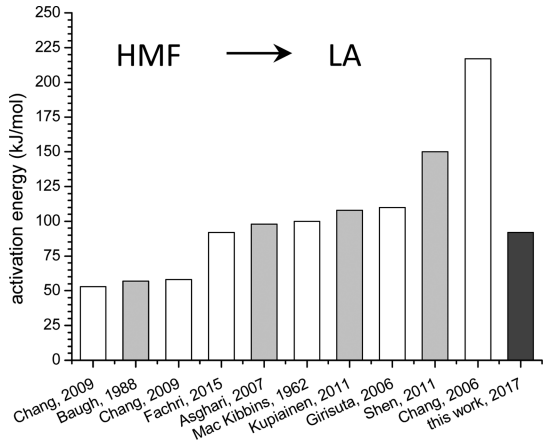


Figure 11. Overview of activation energies for the Brönsted acid-catalyzed conversion of HMF to LA in water: (white bars) using sulfuric acid catalyst; (gray bars) other acid catalysts; (black bar) this study.

1. The alternative reaction networks (2 and 3) are schematically given in Table 4.

The reaction network for model 2 is similar to that for model 1, the only difference is the use of a power law approach to describe the kinetics of humin formation (eqs 25−27) instead of a first order approach. This approach was selected as previous studies with the individual sugars showed that an order higher than 1 gave a better model fit, rationalized by considering that humin forming reactions are intermolecular condensation reactions which are likely not first order reactions.[8,40]

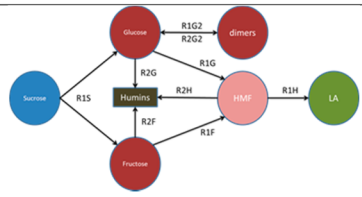
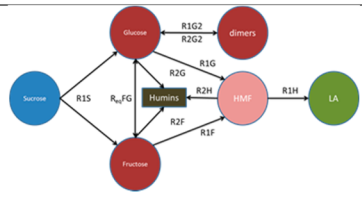
$$R_{2F} = k_{2F}(C_{FRC})^{aF}(C_{H^+}) \quad (25)$$

$$R_{2G} = k_{2G}(C_{GLC})^{aG}(C_{H^+}) \quad (26)$$

$$R_{2H} = k_{2H}(C_{HMF})^{aH}(C_{H^+}) \quad (27)$$

The data set was modeled including the three additional parameters representing the orders in humin formation (aF, aG, aH). The values for the three parameters were 1.6 ± 0.2, 1.5 ± 1, and 0.94 ± 0.1 for aF, aG, and aH, respectively (Table

Table 4. Reaction Networks Tested for Kinetic Modeling

Model	Reaction network	R^2		AIC[62]
1		Overall	0.97782	-6951.9
		LA	0.98456	
		Sucrose	0.99379	
		Glucose	0.98150	
		Fructose	0.96038	
		HMF	0.89693	
2	Model 1 with a power law approach for the orders in humin formation	Overall	0.97771	-6947.5
		LA	0.98414	
		Sucrose	0.99379	
		Glucose	0.98131	
		Fructose	0.96072	
		HMF	0.89628	
3		Overall	0.97771	-6947.6
		LA	0.98409	
		Sucrose	0.99379	
		Glucose	0.98137	
		Fructose	0.96038	
		HMF	0.89789	

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S1, Supporting Information). The quality of the model as expressed in terms of R^2 and the AIC criterion[64] was not much better than that of model 1 (Table 4). In addition, the value for aH is close to 1 and the value for aG has a large confidence interval including 1. As such, and also considering the fact that a model with the lowest number of parameters is preferred, model 2 does not provide a considerable improvement.

In model 1, glucose−fructose isomerization is not included, rationalized by the observation that the acid-catalyzed reaction is known to be much slower than the base-catalyzed isomerization reaction.[43] To assess the importance of isomerization, the glucose−fructose isomerization reaction is included in model 3 (see Table 4 for details).

$$R_{1eq} = k_{1eq}\left((C_{GLC}) - \left(\frac{C_{FRC}}{K}\right)\right)(C_{H^+}) \quad (28)$$

The reaction was modeled as an equilibrium reaction (eq 28) with a first-order dependency in both glucose and fructose. The value of the equilibrium constant (about 1 in the temperature window of this study) was taken from the literature[41,65] and as such only the rate of one of the reactions was fitted. The model quality, expressed by the R^2-value and the AIC criterion, were close to those for model 1 (Table 4). The modeled value of k_{1eq} was $1.7 \times 10^{-4} \pm 1.0 \times 10^{-3}$ L mol^{-1} min^{-1}, which is a factor of 10 lower than all other rate constants (Table 5). As such, this confirms that the rate of the isomerization reaction is relatively slow compared to the time scale of all other reactions. In addition, the confidence interval is larger than the modeled value of the kinetic constant, also an indication that the kinetic constant may actually be close to zero and thus has limited value. Thus, we can conclude that a reaction network involving glucose-fructose isomerization provides a good representation of the experimental data set, though that the model predicts that the contribution of the isomerization reaction is very limited under the prevailing reaction conditions, in line with experimental findings (*vide supra*).

Table 5. Model Results for Model 3 (Including Glucose−Fructose Isomerization (See Table 4)

k value at 140 °C	model result	±	dimension
k_{1G}	0.010	0.002	L mol^{-1} min^{-1}
k_{2G}	0.004	0.002	L mol^{-1} min^{-1}
k_{1F}	0.363	0.015	L mol^{-1} min^{-1}
k_{2F}	0.196	0.020	L mol^{-1} min^{-1}
k_{1HMF}	0.226	0.009	L mol^{-1} min^{-1}
k_{2HMF}	0.030	0.020	L mol^{-1} min^{-1}
k_{1G2}	1.004	0.231	L^2 mol^{-2} min^{-1}
k_{2G2}	3.095	0.814	L mol^{-1} min^{-1}
k_{1eq}	1.7×10^{-04}	1.0×10^{-03}	L mol^{-1} min^{-1}
Ea_{1G}	156	16	kJ mol^{-1}
Ea_{2G}	167	31	kJ mol^{-1}
Ea_{1F}	117	3	kJ mol^{-1}
Ea_{2F}	119	6	kJ mol^{-1}
Ea_{1HMF}	92	3	kJ mol^{-1}
Ea_{2HMF}	138	30	kJ mol^{-1}
Ea_{1G2}	48	11	kJ mol^{-1}
Ea_{2G2}	89	15	kJ mol^{-1}
Ea_{eq}	2	2	kJ mol^{-1}

3.3. Model Implications. *3.3.1. Determination of Optimum Conditions for LA and HMF Yield in Batch.* The model implication calculations were all carried out using model 1, thus assuming that all reactions in the model are first order in reactants and acid concentration, except for glucose reversion. Figure 12 shows the yield of LA as a function of time for different temperatures, at a sucrose starting concentration of 0.1 M and an acid concentration of 0.5 M.

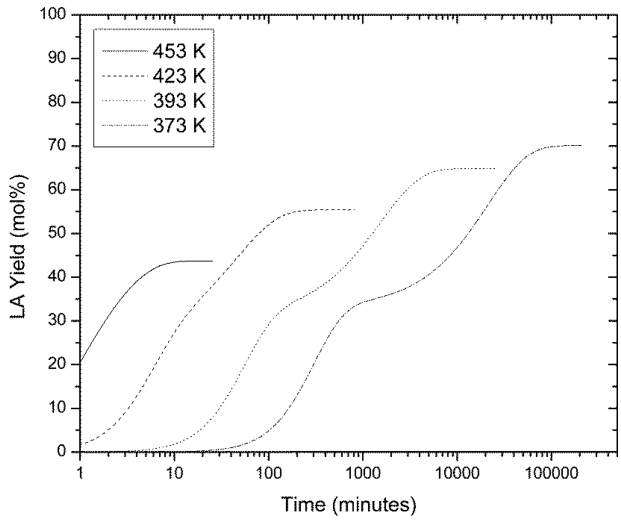

Figure 12. Modeled LA yield as a function of batch time at different temperatures (initial sucrose concentration of 0.1 M, sulfuric acid concentration of 0.5 M).

The model predicts that the LA yield is highest at the lowest temperature in the range, namely, 70 mol % at 100 °C. This may be rationalized by considering that the reactions leading to humins all have higher activation energies than the reactions forming LA. Therefore, lowering the temperature will lead to higher LA yields. However, the batch times at lower temperatures are excessively longer than at the highest temperature (up to 70000 min for maximum LA yield at 100 °C), leading to very unrealistically low reactor productivities (mol LA·m$^{-3}_{reactor}$·h^{-1}). As such, the optimum temperature for LA synthesis will be a compromise between LA yield and batch time.

The highest experimental value for the yield of LA was 61 mol % at 160 °C, in line with model predictions using the experimental conditions as input. LA yields at lower temperatures were, in contrast to model predictions, lower, which is due to incomplete conversion of particularly glucose, the least reactive sugar, and as such the maximum LA yields were not attained.

The modeled HMF yield versus the temperature is given in Figure 13. The highest modeled HMF yield is 21 mol %, obtained at the highest temperature in the range.

4. CONCLUSIONS

An experimental and kinetic modeling study on the conversion of sucrose to LA and HMF in water using sulfuric acid as the catalyst is reported. The maximum experimental LA yield was 61 mol % (160 °C, an initial sucrose concentration of 0.05 M and an acid concentration of 0.2 M), whereas the maximum HMF yield was 22 mol % (140 °C, an initial sucrose concentration of 0.05 M and an acid concentration of 0.05 M). The experimental data were modeled using a number of possible reaction networks, and the best model when considering model quality indicators (R-squared of parity

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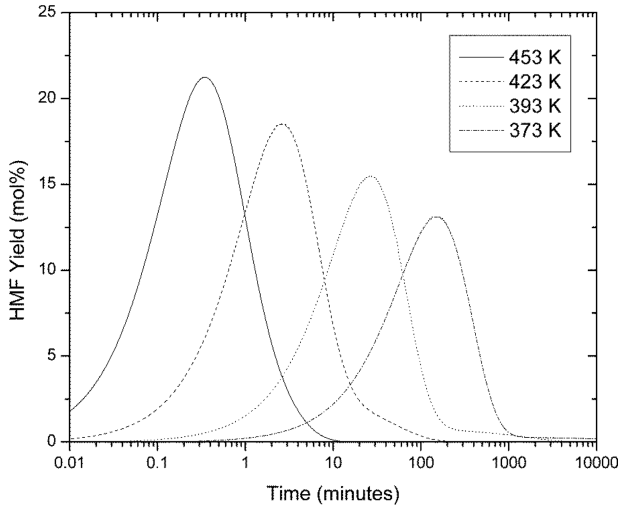

Figure 13. Modeled HMF yield as a function of time at different temperatures (initial sucrose concentration of 0.1 M, sulfuric acid concentration of 0.5 M).

plots, AIC criterion, and number of model parameters) was obtained when using a first order approach in substrates (except for the reversion of glucose). The model was used to determine optimum conditions regarding LA and HMF yields in batch and predicts that highest LA yields are possible at the lowest temperature in the range, though this goes at the expense of reactor productivity (mol LA·$m^{-3}_{reactor}$·h^{-1}) due to considerable reductions in reaction rates. Highest HMF yields are predicted for the highest temperature in the range.

This information may be used to develop efficient processes for the conversion of sucrose solutions to biobased building blocks like HMF and LA. In addition, it may also be the starting point for the development of such processes using waste streams from sugar industries, though experimental studies with such real feeds will be required to assess the effects of impurities (salts, proteins, bases) on rates of the individual reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b01611.

HPLC chromatogram for a typical reaction product using sulfuric acid, and a table with data for the powerlaw model (model 2) (PDF)

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Notes

The authors declare no competing financial interest.

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