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Research Article

5-Hydroxy-2-Methylfurfural from Sugar Beet Thick Juice: Kinetic and Modeling Studies

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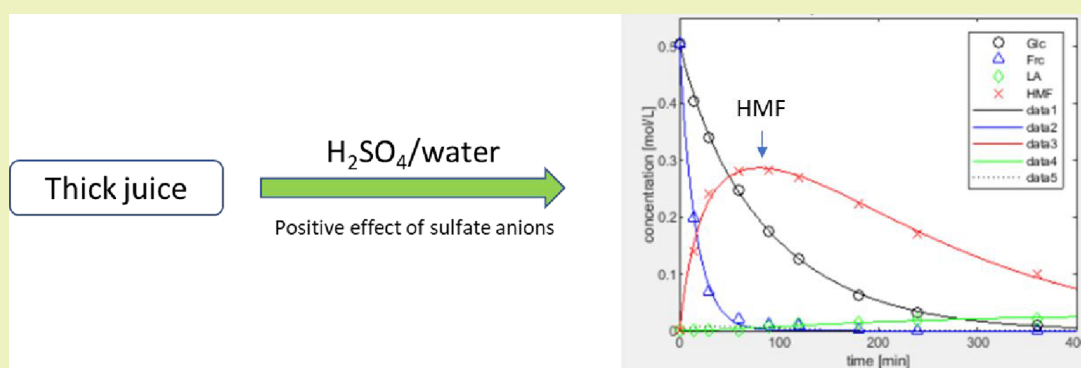Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 2626−2638

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ABSTRACT: 5-Hydroxy-2-methylfurfural (HMF) has a high derivatization potential and is considered the sleeping giant of biobased platform chemicals. It is accessible by the acid hydrolysis of various carbohydrate-containing feeds, preferably those high in fructose content. We here report a detailed study on the use of thick juice, an intermediate sucrose (SUC)-rich stream in a sugar factory, and pure SUC for the synthesis of HMF in a batch reactor setup [in the presence of water and sulfuric acid (0.01 M) and at 180 °C]. Distinct differences in reactivity were found for both feeds, related to the presence of impurities (i.e., organic acids and salts) in the thick juice. To better understand the effect of the thick juice impurities, detailed model studies were performed involving the use of a model solution of SUC spiked with one of the thick juice impurities (organic acids such as maleic acid and a range of salts with potassium, sodium, calcium, and magnesium as the cations and carbonates, chlorides, and sulfates as the anions). The data were successfully modeled using a kinetic model for the main reactions in the network. The developed model revealed that sulfate anions have a major effect on the HMF yield and the batch time required to reach its optimum and are the likely cause of the differences in reactivity between pure SUC and thick juice.

KEYWORDS: biobased chemicals, HMF, thick juice, kinetics, sulfate effects

■ INTRODUCTION

Environmental issues related to the use of fossil resources have led to extensive efforts to identify alternative feedstocks for chemical products. Of all options, biomass is considered an attractive feed for the production of more sustainable fuels and chemicals.[1−4] Among the many chemicals that may be derived from biomass, 5-hydroxy-2-methylfurfural (HMF) is considered very attractive. It is accessible by an acid-catalyzed hydrolysis reaction of saccharides, both monomeric and polymeric in nature. Among the saccharides investigated,[2,5−8] fructose (FRC) is known to be the most suitable one in terms of HMF yields, and under aqueous acidic conditions, HMF yields of up to 50% have been reported. In contrast, when using abundantly available glucose (GLC) in water, HMF yields are typically below 10%.[9] Major byproducts during HMF synthesis from these carbohydrates are insoluble polymers known as humins, as well as the small organic acids levulinic acid (LA) and formic acid (FA).

Sucrose (SUC), produced globally in large volumes from either sugar beets or sugar cane, is a disaccharide consisting of FRC and GLC. It has been tested as a feed for HMF synthesis[6,10] and an overview of the Brønsted acid-catalyzed conversion of SUC to HMF in water is provided in Table S1 (Supporting Information). Recently, we have reported a comprehensive study on the conversion of SUC into HMF and LA using sulfuric acid in water in the temperature range of
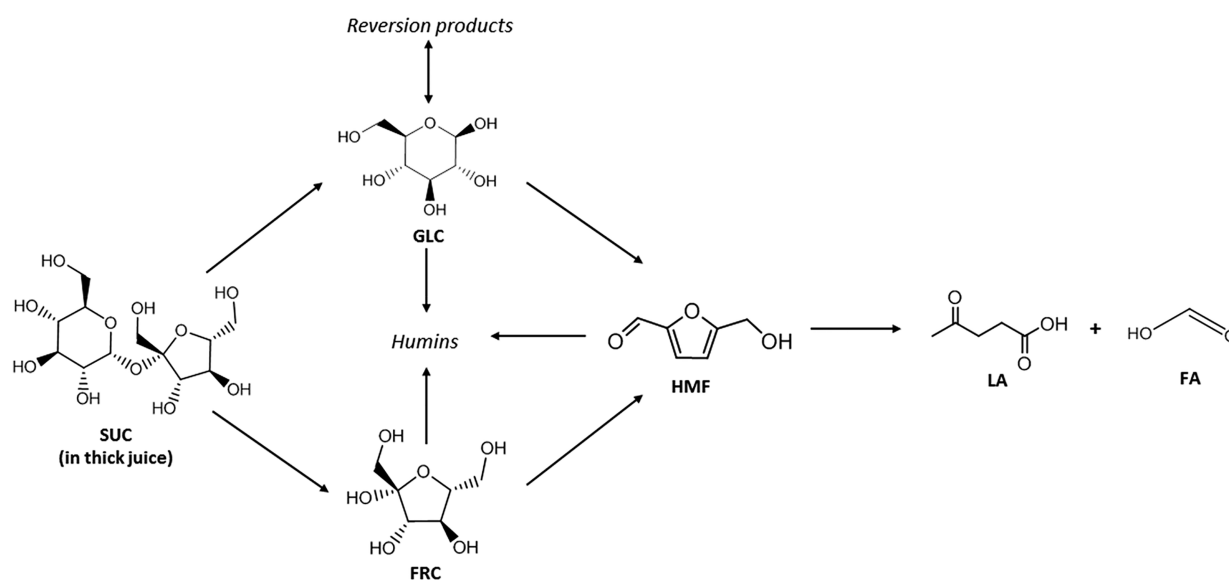
Scheme 1. Proposed Reaction Scheme of SUC in Thick Juice Conversion to 5-Hydroxymethyl-2-Furfural (HMF) and Levulinic Acid (LA)

80−180 °C.[9] A reaction network was proposed involving the rapid hydrolysis of SUC to give FRC and GLC, followed by FRC dehydration to HMF, with concomitant formation of LA, FA, and the (solid) humins[11−13] (Scheme 1).

We have also recently demonstrated the use of thick juice for the synthesis of HMF in a biphasic reaction system[14] and showed that HMF yields >90% (calculated on FRC basis) are possible in a microreactor setup at 150 °C (with H_2SO_4 as a catalyst and 2-methyltetrahydrofuran as a bioderived extraction solvent). Thick juice is a SUC-rich intermediate product stream produced in sugar factories (see Supporting Information, Figure S2) and contains, besides water and SUC (about 65 wt %), impurities such as organic acids and salts (Table 1). Typical cations are Ca^{2+} and K^+, in combination with anions like Cl^- and SO_4^{2-}.

The use of thick juice in the biphasic system instead of pure SUC led to significantly higher HMF yields,[14] and it was proposed that the impurities present in the thick juice have a positive effect, though the exact cause remained unclear. In this work, we present a model study in a batch reactor setup using water as the solvent and sulfuric acid as the catalyst and SUC, either pure or in the presence of impurities typically present in the thick juice (i.e., organic acids and salts). The performance in terms of FRC reactivity and HMF yield was compared with that of thick juice to get further insight into which impurities cause this positive effect. The experimental data were modeled using a reaction network earlier proposed by us for pure SUC,[9] and this allowed for quantification of the kinetic rate constants for the relevant reactions. With this information, it was shown that particularly the presence of salts with sulfate anions has a major effect and is the likely cause of the differences observed between pure SUC and thick juice. The effect of impurities on the efficiency of catalytic biomass conversion processes is often considerable and requires more attention. With this example, we show that these effects do not always have to be detrimental and that the use of crude feedstock can also bring unexpected advantages.

■ EXPERIMENTAL SECTION

Materials. Thick juice was kindly provided by Suiker Unie-Royal Cosun. Sulfuric acid (96−98 wt %), SUC (≥ 99 wt %), GLC (≥ 99.5 wt %), FRC (99 wt %), NaCl, $CaCO_3$, $MgCl_2$, and FA were obtained from Sigma-Aldrich (Steinheim, Germany). K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCl_2$, and KCl were acquired from Merk Millipore (Darmstadt, Germany). LA was purchased from Alfa Aesar. All chemicals were used without further purification. For all experiments, Milli-Q water was used to prepare the solutions.

SUC Content in Thick Juice. The SUC content of the thick juice solution used for the experiments was determined by polarimetry (see section 2.4). This method is a suitable alternative for routine high-performance liquid chromatography (HPLC), for which accurate SUC analyses are difficult because of SUC hydrolysis to GLC and FRC in the HPLC column when using a typical acidic mobile phase. According to polarimetry, the thick juice used in this study consists of 62 wt % SUC (about 2 M). To test the validity of this method, the thick juice was also hydrolyzed under very mild conditions (5 mM H_2SO_4, 100 °C, and 0.5 g thick juice in 10 mL), and the changes in GLC and FRC concentration over time were determined. The GLC and FRC concentrations became about constant after 60 min, and both were found to be present in equimolar amounts. From the GLC and FRC concentration, the SUC concentration in the original thick juice was calculated and found to be 62 ± 1 wt %, which is close to

Table 1. Literature Data on the Composition of Thick Juice

|	Tan et al.[15]		Van Zandvoort[16]
lactic acid (mg/L)	13,586 ± 545.9	Zn^{2+} (wt %)	< 0.0002
acetic acid (mg/L)	2176 ± 117.4	Al^{3+} (wt %)	< 0.0002
sucrose (g/L)	640.3 ± 23.8	Mn^{n+} (wt %)	< 0.0002
glucose (g/L)	87.9 ± 6.4	Fe^{3+} (wt %)	< 0.0002
fructose (g/L)		K^+ (wt %)	0.6−0.8
NH_4^+ (mg/L)	104.6 ± 3.8	Na^+ (wt %)	0.1
Ca^{2+} (mg/L)	1568 ± 73.5	malic acid (wt %)	0.02−0.1
Mg^{2+} (mg/L)	110.6 ± 7.4	lactic acid (wt %)	0.2−0.5
K^+ (mg/L)	5432 ± 63.6	acetic acid (wt %)	0.1
		pyrrolidone carboxylic acid (wt %)	0.2
		citric acid (wt %)	0.02−0.1
		sucrose (wt %)	60−70
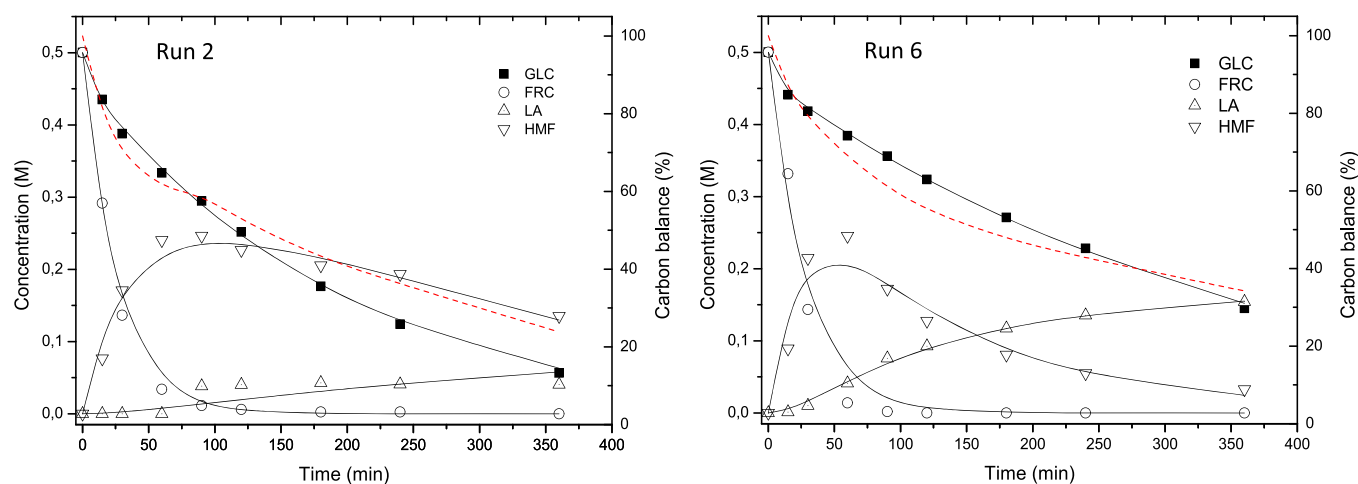
Figure 1. Concentration−time profiles for thick juice (left, run 2) and pure SUC (right, run 6). Reaction conditions: $C_{SUC(equivalent),0}$ = 0.5 M, T = 180 °C. Initial pH = 3.8 for thick juice and 3.7 for pure SUC. Red dashed lines represent carbon balances. Solid lines represent model values. Run numbers refer to data in Table 3 and Figure S5.

the value obtained with polarimetry. This value was confirmed by direct measurement of the SUC content in thick juice by high-performance anion-exchange chromatography on a Dionex Ultimate 6000 system equipped with a CarboPac PA-1 column (see Supporting Information for more details).

Batch Experiments in Water. The experimental methods for the experiments in water are based on published work by Girisuta et al.[17] The reactions were carried out in glass ampoules with an internal diameter of 3 mm, a wall thickness of 1.5 mm, and a length of 15 cm. A total of eight ampoules were used for one series of experiments. The ampoules were loaded with approximately 0.3 mL of the reaction mixture consisting of a predetermined amount of thick juice (about 0.5 M of SUC equivalent) or SUC (0.5 M) and catalyst (0−0.1 M sulfuric acid). The ampoules were then sealed with a torch and arranged in an aluminum rack before being subsequently placed in a temperature-controlled oven (GC oven, Hewlett Packard 5890A) at T = 180 °C. At different reaction times, an ampoule was removed and immediately submerged in cold water to quench reactions. Afterward, the ampoules were opened and the reaction mixture was withdrawn. The mixture was filtered over a PTFE filter (0.45 μm) to remove any insoluble matter. Subsequently, an aliquot of the clear solution was taken (28 μL) and diluted with Milli-Q water (1672 μL). The obtained sample was analyzed by HPLC.

Analytical Methods. *Polarimetry.* The SUC content in thick juice was determined using polarimetry. A series of SUC solutions with known concentrations were prepared, and the observed rotation (α_{obs}) of each solution was obtained using a polarimeter (Schmidt + Haensch, Polatronic MH8). The wavelength (λ) and cell length were 589.44 and 100 mm, respectively. With this data set, the specific rotation of SUC ($[\alpha]$) was calculated (see Supporting Information for details). The SUC concentration in the original thick juice was calculated by measuring the optical rotation of a thick juice solution with a known dilution factor.

pH Measurements. The pH of the reaction mixtures was measured at room temperature using an InoLab pH 730 pH-meter equipped with a SenTix 81 probe (both probe and meter from WTW, Germany).

High-Performance Liquid Chromatography. The composition of the aqueous phase after the reaction was determined by HPLC. The instrument consists of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), a refractive index detector, and a UV detector. The HPLC column was operated at 60 °C, and an aqueous sulfuric acid (5 mM) solution was used as the mobile phase with a flow rate of 0.55 mL min^{-1}. The injection volume was set at 5 μL. The concentrations of individual compounds in the product mixture were determined using calibration curves obtained by analyzing standard solutions of known concentrations.

Definitions. The concentrations of the relevant compounds involved in the reaction were determined by HPLC. These concentrations were used to calculate the conversion of SUC (X_{SUC}) and the yield of HMF (Y_{HMF}) according to the definitions given in eqs 1 and 2.

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

$$Y_{HMF} = \frac{C_{HMF}}{2C_{SUC,0}} \tag{2}$$

Here, $C_{SUC,0}$ is the initial concentration of SUC. All definitions are on a molar basis. The carbon balance closure is defined as the total moles of carbon in HPLC detectable compounds (FRC, GLC, HMF, FA, and LA) at certain reaction time divided by the moles of carbon in the feed (eq 3).

$$\text{Carbon balance closure}$$
$$= \frac{\text{mol C in HPLC detectable compounds}}{\text{mol C in the feed}} \times 100\% \tag{3}$$

Kinetic Modeling. A kinetic model for the reactions of SUC and thick juice in water with sulfuric acid as the catalyst was developed based on the reaction mechanism provided in Scheme 1. This scheme was also featured in a previous kinetic study performed in the Groningen group for pure SUC.[9] The kinetic parameters were determined using a nonlinear least-squares approach using the MATLAB function lsqnonlin, which is based on a trust-region reflective algorithm and involves minimization of the errors between the experimental data and the kinetic model.

RESULTS AND DISCUSSION

Benchmark Experiments in Water with Thick Juice and SUC. The thick juice experiments were carried out in a batch reactor at a small scale (0.3 mL liquid intake) at 180 °C, with H$_2$SO$_4$ as the catalyst (0.01 M) and an initial thick juice loading corresponding to 0.5 M SUC. The pH of the solution was measured and found to be about 3.8 at room temperature. The product distribution versus reaction time for a typical 6 h run is shown in Figure 1 (left side). SUC is rapidly converted into FRC and GLC, and actually, SUC could not be detected in the first sample (15 min). Both FRC and GLC are converted in the course of the reaction, though it is clear that FRC is by far more reactive than GLC, in line with literature data.[9,14] The maximum HMF yield was 24.6 mol % at 90 min batch time. At

Scheme 2. Reaction Network Used for Kinetic Modeling with SUC, Sucrose, FRC, Fructose, GLC, Glucose, HMF, 5-Hydroxy-2-Methylfurfural, and LA, Levulinic Acid
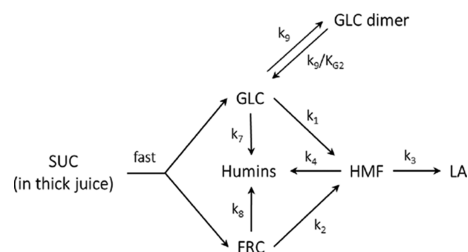

Table 2. Rate Equations Used in the Kinetic Model Based on Scheme 2

reaction	reaction rate
GLC → HMF	$r_1 = k_1 C_{GLC}$
FRC → HMF	$r_2 = k_2 C_{FRC}$
HMF → LA	$r_3 = k_3 C_{HMF}$
HMF → Humins	$r_4 = k_4 C_{HMF}$
GLC → Humins	$r_7 = k_7 C_{GLC}$
FRC → Humins	$r_8 = k_8 C_{FRC}$
2GLC → GLC dimer	$r_9 = k_9 C_{GLC}^2 - \dfrac{k_9}{K_{G2}} C_{G2}$

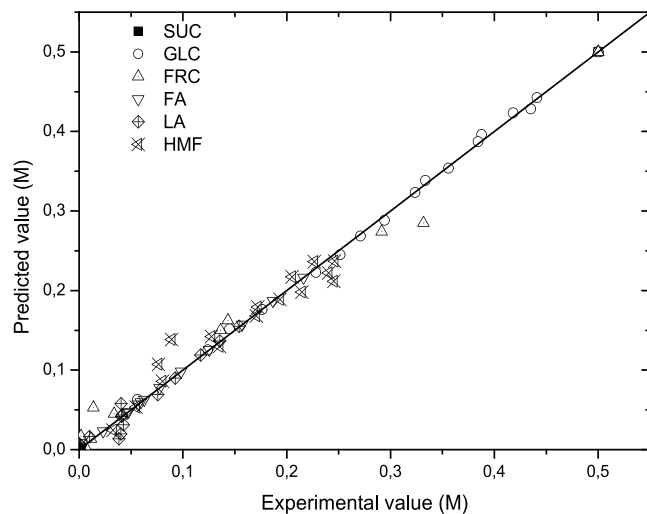| component	component production rate
GLC	$R_{GLC} = -r_1 - r_7 - 2r_9$
FRC	$R_{FRC} = -r_2 - r_8$
HMF	$R_{HMF} = r_2 - r_3 - r_4$
LA	$R_{LA} = r_3$
GLC dimer	$R_{G2} = r_9$

Figure 2. Parity plot for experimental and modeled data for the benchmark experiments with SUC, sucrose, FRC, fructose, GLC, glucose, FA, formic acid, LA, levulinic acid, and HMF, 5-hydroxy-2-methylfurfural.

longer reaction times, the HMF concentration gradually decreased and LA and FA (not shown) are formed. The carbon balance based on HPLC detectables at the end of the reaction is far from quantitative (Figure 1), indicating that substantial amounts of non-HPLC detectables, likely soluble and solid humins, are formed. In line with this statement is the observation that the carbon balance closure is time-dependent, with better closures at the start of the reaction. Humin formation is also clear from the visual appearance of the
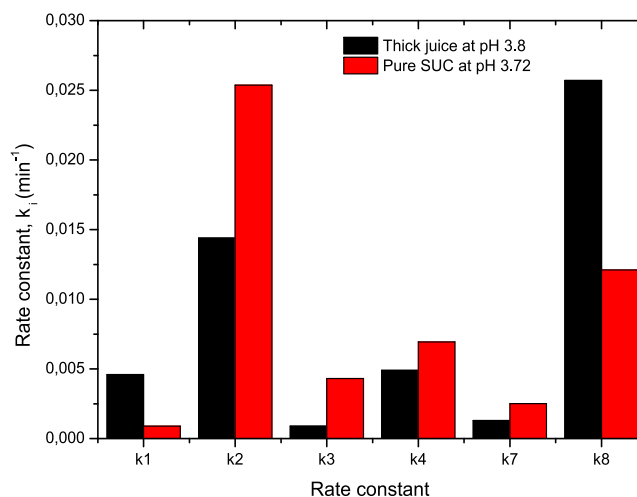

Figure 3. Kinetic constants for thick juice and pure sucrose (SUC) for the benchmark experiments (reaction conditions: $C_{SUC(equivalent),0} = 0.5$ M, T = 180 °C, sulfuric acid as the catalyst)

reaction mixture during the reaction, changing from clear/transparent yellow to brown as well as the formation of small-sized brown/black solids (see Figure S3 in the Supporting Information for more details).

For comparison, an experiment with pure SUC was performed at a similar pH value as used for thick juice (3.7), and the results are given in Figure 1 (right side). Distinct differences in the concentration−time profiles between thick juice and pure SUC were observed. In both cases, FRC is converted at essentially the same rates, whereas GLC is less reactive in the case of SUC. The highest HMF concentration for SUC is lower than for thick juice, confirmed by subsequent kinetic modeling activities (vide infra). Besides, the HMF concentration profile shows a sharper maximum for the pure SUC reaction, in contrast to the shallower one found for thick juice. This implies that the rate of conversion of HMF into LA and humins is much higher for SUC than for thick juice. In line with this observation is a higher amount of LA at the end of the reaction. The carbon balance for the SUC reaction is, as for thick juice, far from quantitative, though slightly better than for thick juice.

Kinetic Modeling. The concentration−time profiles for the individual components for the benchmark experiments with thick juice and SUC were modeled to obtain the kinetic constants of the individual reactions in the network. All data were obtained at 180 °C, and as such, only the values for the kinetic parameters (k values) were derived, without an Arrhenius dependency. This approach provides quantitative information, which will be used to determine the difference in using thick juice or SUC for HMF synthesis. The kinetic model used for this purpose is given in Scheme 2 and is based on a kinetic model developed earlier in the Groningen group for pure SUC reactions in water (Scheme 1).[9] The reaction rates of each component are given in Table 2.

As SUC almost instantaneously inverts to GLC and FRC in a 1 to 1 molar ratio at 180 °C,[9] the rate of this reaction is not included in the model. This was confirmed by performing separate experiments with SUC (0.5 M) at 180 °C. After 2 min, no SUC was present in the mixture, implying full conversion at a small time scale (Figure S1, Supporting Information). Also, all reactions are considered to be first-order reactions in the substrate, the only exception being the

Table 3. Experimental Details on Thick Juice and Sucrose (SUC) Reactions[a]

run	starting material	initial pH	H_2SO_4	additives	Y_{HMF} max[d] (mol%)	t at Y_{HMF} max[e] (min)
1	thick juice	8.5			22.6	161
2[b]	thick juice	3.8	0.01 M		27.2	106
3	thick juice	1.88	pH adjusted with H_2SO_4		28.5	45
4	SUC	5.7			25.5	58
5	SUC	1.8	0.01 M		30.2	12
6[b]	SUC	3.72	pH adjusted with H_2SO_4		26.2	58
7	SUC	11.17	pH adjusted with KOH		13.7	228
8[c]	SUC	1.75	0.01 M	citric, malic, oxalic, lactic, acetic acid and PCA[e]	29.2	12
9[c]	SUC	2.7		citric, malic, oxalic, lactic, acetic acid and PCA[e]	26.6	50
19	SUC	3.75	0.01 M	$CaCO_3$ (1 mg mL^{-1})[c]	30.2	85
20	SUC	3.7	0.01 M	Na_2CO_3 (1 mg mL^{-1})[c]	33.6	108
21	SUC	3.76	0.01 M	K_2CO_3 (1 mg mL^{-1})[c]	34.0	112
22	SUC	3.72	0.01 M	$MgCO_3$ (1 mg mL^{-1})[c]	32.8	92
23	SUC	1.95	0.01 M	$CaCl_2$ (1 mg mL^{-1})[c]	30.2	11
24	SUC	1.93	0.01 M	NaCl (1 mg mL^{-1})	31.0	11
25	SUC	1.98	0.01 M	KCl (1 mg mL^{-1})	29.5	19
26	SUC	1.96	0.01 M	$MgCl_2$ (1 mg mL^{-1})[c]	30.5	10
27	SUC	2.2		0.01 M Maleic acid	29.0	26
29	SUC	1.74	0.01 M	0.006 M KNO_3	29.5	13
30	SUC	1.80	0.01 M	0.01 M Na_2SO_4	26.2	37
31	SUC	2.18	0.01 M	0.05 M Na_2SO_4	34.4	85
32	SUC	2.29	0.01 M	0.1 M Na_2SO_4	33.4	81
33	SUC	1.98	0.01 M	0.01 M K_2SO_4	26.2	43
34	SUC	2.3	0.01 M (with HCl)	0.05 M Na_2SO_4	30.1	86
35	SUC	2.47	0.01 M (with HCl)	0.1 M Na_2SO_4	29.5	81

[a]All runs were done at T = 180 °C with initial feed concentration, $C_{SUC(equivalent),0}$ = 0.5 M. [b]Benchmark experiment (Figure 1). [c]Amounts based on the values reported in the literature (Table 1) for thick juice. [d]Simulated values based on the kinetic model; calculation procedures are given in the Supporting Information. [e]Pyrrolidone carboxylic acid.

conversion of GLC into reversion products such as GLC oligomers and anhydrosugars. At high sugar loadings (> 200 mg/mL), up to 12 wt % of GLC is converted to reversion products, which are mainly disaccharides.[18] As such, reversion chemistry is simplified by assuming that GLC is converted to a GLC dimer and has a second-order dependency in GLC. Additionally, this reaction is also known to be reversible and reversibility was also considered in the model.[18] The value for the equilibrium constant (K_{G2}) for the reaction was taken from the literature.[9]

It is also assumed that both FRC and GLC react independently to HMF, which is based on literature evidence for kinetic studies on SUC in the Groningen group,[9] studies using GLC only[17] and for FRC-GLC mixtures in water-acetone.[19] As such, the existence of an equilibrium reaction between FR and GLC was not included in the model. Finally, it is assumed that GLC, FRC, as well as HMF form soluble and insoluble humins, whereas cross-condensation reactions between the sugars and sugars/HMF do not occur to a significant extent.[9]

Using these assumptions, an excellent fit between data and model was obtained (see Figure 1 for details), confirmed by a parity plot showing the experimental and modeled concentrations of the main products (Figure 2). The individual k values for the benchmark experiments with thick juice and SUC are given in Figure 3, showing remarkable differences between the two feeds.

When considering the relevant kinetic constants associated with HMF formation/disappearance (k_2, k_3, and k_4), these are all higher for SUC than for thick juice. These findings imply that the FRC and its product HMF react much faster when

using pure SUC compared to thick juice, as also observed experimentally. The only exceptions are k_1 and k_8, which are lower for SUC than for thick juice. The former is related to the reaction involving GLC (GLC to HMF), suggesting that GLC is less rapidly converted to HMF when using pure SUC, which is in line with the experimental observations (Figure 1). Rate constant k_8 is associated with FRC conversion to humins, which is lower for SUC than for thick juice. The k values for GLC inversion to dimers (k_9) were considerably higher than the other kinetic constants in the reaction network for both feeds (see Supporting Information, Table S2 for details) and therefore not included in Figure 3.

Model Studies on the Effect of Minor Components in the Thick Juice. The differences in the reaction rate constants of the individual reactions in the reaction network must originate from the difference in composition between thick juice and SUC (Table 1). Thick juice contains, besides SUC, considerable amounts of salts, organic acids, and other minor components (see Table 1). All these compounds may affect the rate of the individual reactions in the network. Besides, thick juice is basic, and as such, the pH of the reaction mixture may also play a role. To systematically investigate the effect of pH, organic acids, and salts on the individual reaction rates in the network, several experiments were performed with model solutions of SUC spiked with various components present in thick juice in considerable amounts (acids and salts; see Table 3 for details). Some of the experiments were performed in duplicate and show good reproducibility (see Supporting Information, Figures S3).

pH Effects. To investigate pH effects on the rates of the individual reactions in the developed network, seven experi-
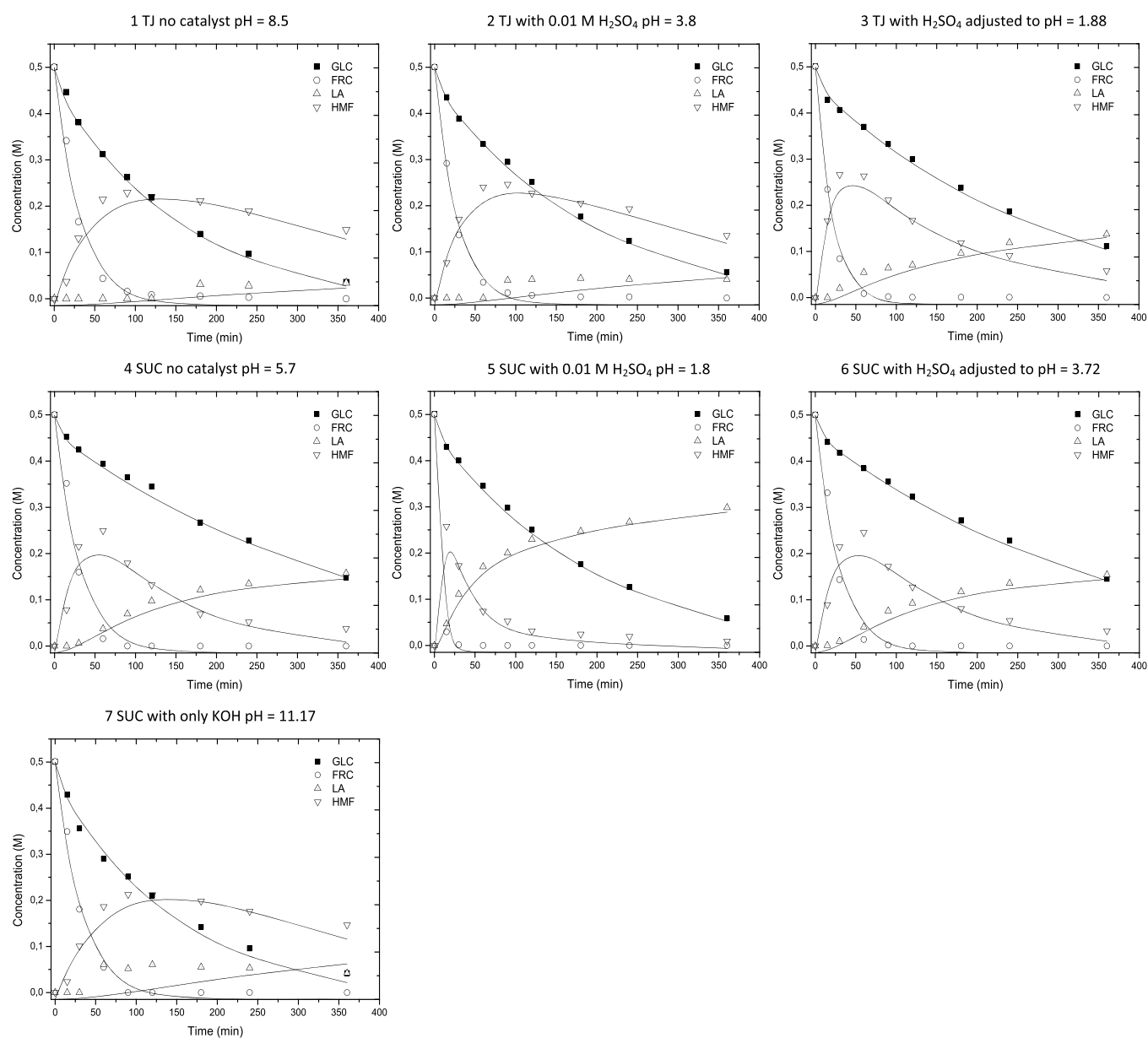
Figure 4. Concentration−time profiles for thick juice (TJ) and pure sucrose (SUC) at different pH values. Reaction conditions: $C_{SUC(equivalent),0}$ = 0.5 M, T = 180 °C. The solid lines represent model values, while the numbers above the graphs correspond to the run numbers in Table 3.

ments at different initial pH values (1.9−11.2) and constant temperature (180 °C) were performed. Three experiments were conducted with thick juice (Table 3, runs 1−3) and four with pure SUC (Table 3, runs 4−7). The concentration versus time profiles of these experiments including the model lines are presented in Figure 4.

Qualitatively, the curves for both feeds differ considerably, both in terms of the rate of FRC conversion and the shape of the HMF concentration−time profile. To obtain quantitative information, the kinetic constants for the individual reactions were determined using the kinetic model, and the results for the main reactions involving FRC (reactions 2, 3, and 4, see Scheme 2) are given in Figure 5 and Table S2 (Supporting Information).

For thick juice, the pH in the range 3.8−8.5 has a relatively small effect on the values of the kinetic constants. However, for an experiment at the lowest pH value (1.8, run 3), the value for k_2 (FRC to HMF) is significantly higher than for the

experiments at higher pH values. For SUC, a similar trend is observed and the pH has a small effect in the pH range 4−6, whereas it is considerably increased at a low pH value of 1.8. A similar pH trend was found by Kusters et al.[20] in a study on the conversion of FRC to HMF in water at 175 °C in a stirred tank reactor. Here, the kinetic constant of the rate of the reaction of FRC to HMF (k_2) also showed a significant increase in value when the pH was below 2. The effect of the acidity on the value of k_2 within the SUC reaction network was visualized by plotting the k_2 value versus the $[H^+]$ (see Figure S6, Supporting Information). A linear relationship between the $[H^+]$ and the observed rate constant was observed, as expected for Brønsted acid catalysis.

Of interest is also the observation that in the basic regime, at pH = 11.2, SUC is still converted to the same products as found for acidic conditions, indicating that the chemo-selectivity of the thermal conversion of FRC to HMF is not
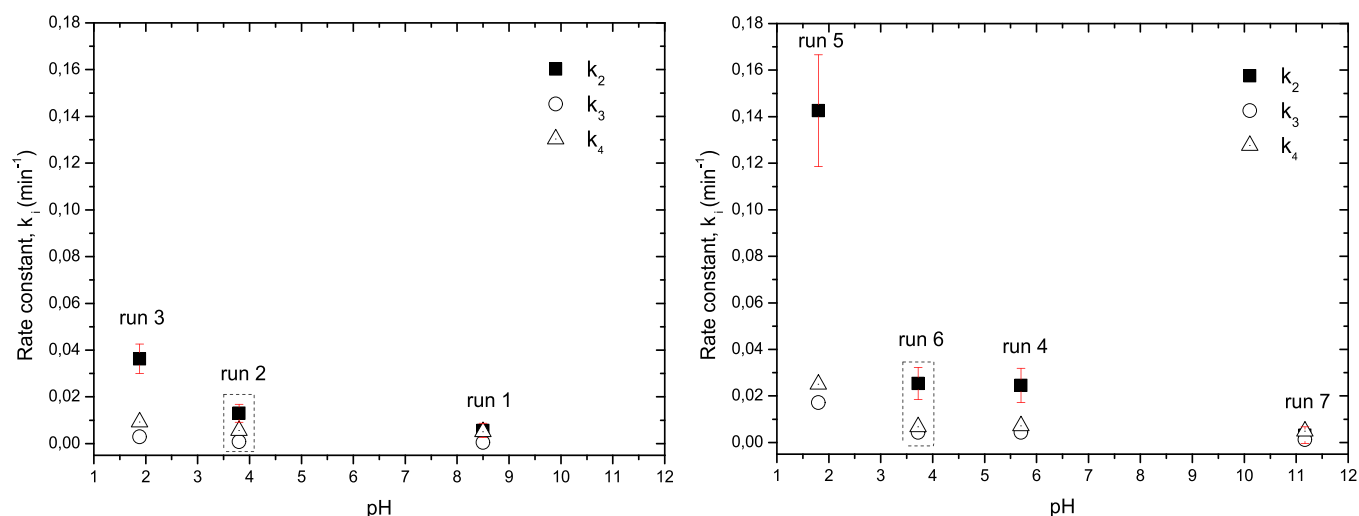
Figure 5. Rate constants for main reactions involving 5-hydroxy-2-methylfurfural (HMF) versus pH. Left side: thick juice experiments 1−3; right side: pure sucrose SUC (4−7). Data in the box (pH 3.7−3.8) are for the benchmark experiments.
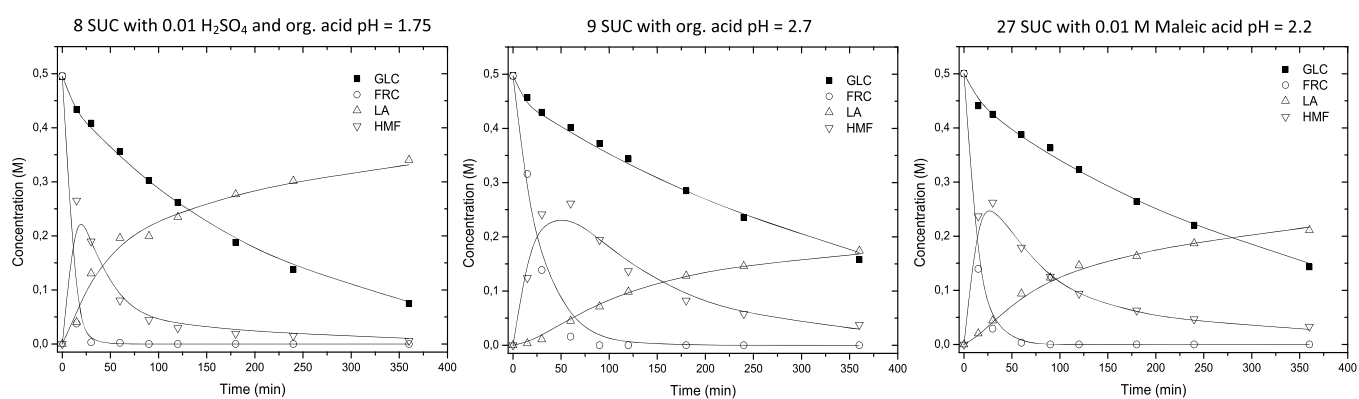

Figure 6. Concentration−time profiles for sucrose (SUC) hydrolysis in the presence of various organic acids. Reaction conditions: $C_{SUC(equivalent),0}$ = 0.5 M, T = 180 °C. The solid lines are model values, while the numbers above the graphs correspond to the run numbers in Table 3.
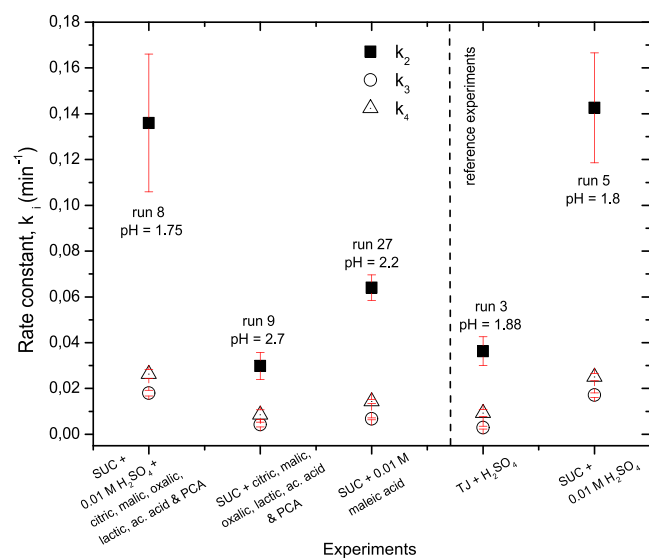

Figure 7. Relevant rate constants for various sucrose (SUC) reactions in the presence of organic acids.

significantly changed when switching from acidic to slightly basic conditions.

Taken together, these experiments clearly show the pH to have a strong effect over the ranges studied (1.9−11.2) on the values of the kinetic constants for the relevant reactions and as such affect the concentration−time profiles of the products. Thus, pH effects should be considered when comparing the data.

Effects of Organic Acids. Thick juice contains various organic acids (see Table 1 for details), impurities that may affect the rates of the individual reactions in the reaction network. To investigate their effect, several SUC experiments (180 °C, 0.5 M SUC) were conducted in the presence of representative organic acids (Table 3, runs 8, 9, and 27). Experiments were conducted with a mixture of citric, malic, oxalic, lactic, acetic acid, and pyrrolidone carboxylic acid, and they were added to the SUC solution in amounts similar to those found in thick juice (Table 1) to mimic the thick juice composition (Runs 8 and 9). For run 8, 0.01 M sulfuric acid was also added, whereas no sulfuric acid was added for run 9. One experiment was performed using maleic acid (run 27, no sulfuric acid added), as it is known that particularly maleic acid can have a positive effect on the selectivity of hexose dehydration reaction to HMF.[21]

The concentration−time profiles and the kinetic constants of these experiments are given in Figures 6 and 7, respectively. The modeled kinetic constants for run 8 (organic acids in the
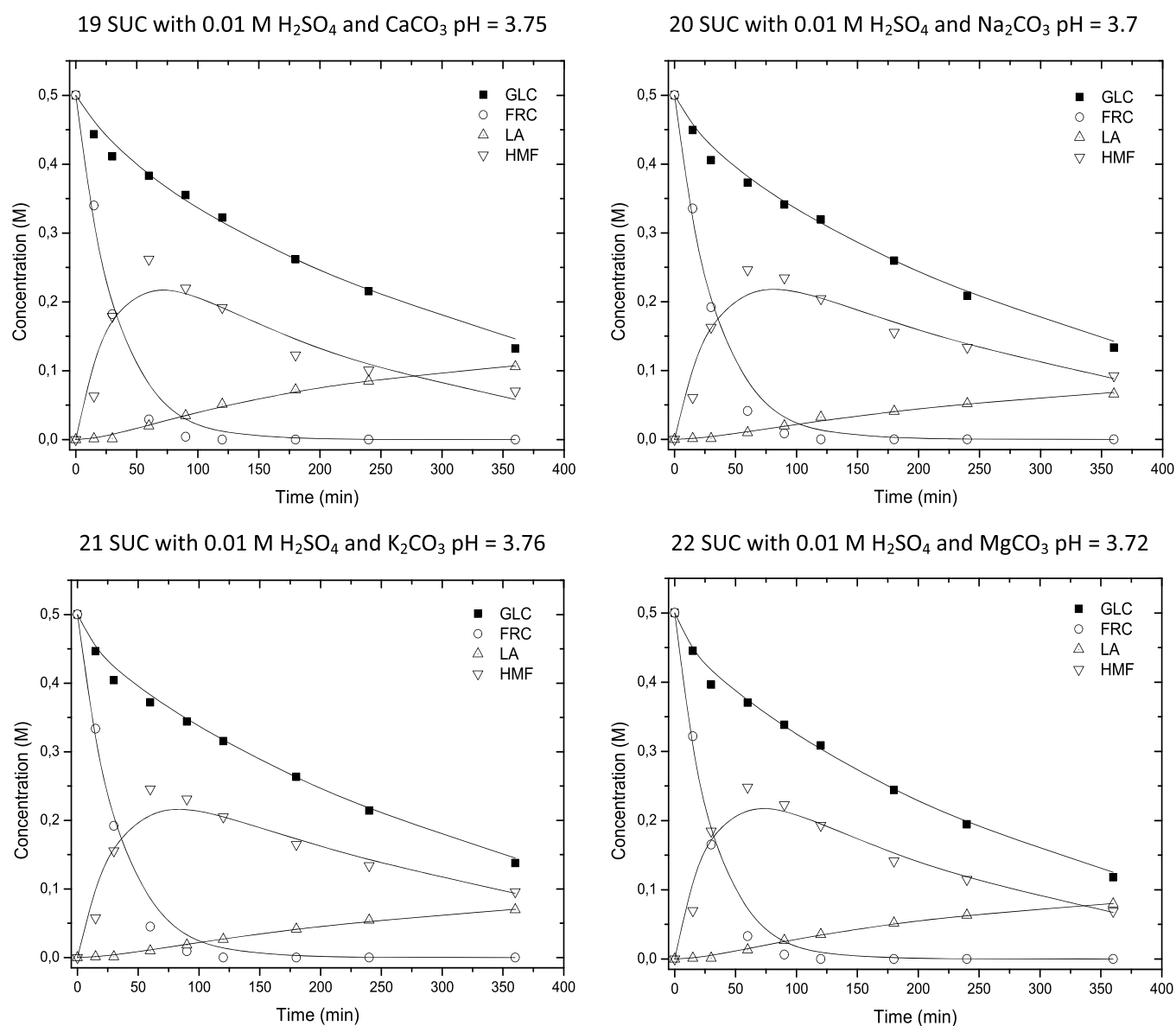
Figure 8. Concentration−time profiles for sucrose (SUC) hydrolysis in the presence of carbonate salts. Reaction conditions: $C_{SUC(equivalent),0} = 0.5$ M, 0.01 M H_2SO_4 T = 180 °C. The solid lines represent model values, while the numbers above the graphs correspond to the run numbers in Table 3.

presence of 0.01 M sulfuric acid, pH 1.8) are essentially similar to those observed for an experiment with SUC with the same amount of sulfuric acid, but without the addition of organic acids (run 5, Table 3, pH = 1.8), thus showing no significant influence of the organic acids. This is most likely because sulfuric acid ($pK_{a,1} = −3$) is by far a stronger acid than the organic ones (lactic acid, 3.85, malic acid, 3.40, acetic acid, 4.8), and as such, the latter are likely fully protonated in solution and have a minor catalytic effect. Therefore, an experiment with the organic acids without sulfuric acid addition was performed (pH 2.7, run 9). Indeed, this resulted in lower rates for the relevant reactions to HMF compared to an experiment in the presence of sulfuric acid. However, the kinetic constants are about similar to those found for the benchmark SUC experiment at pH 3.7 and higher than those found for thick juice at pH 3.8. Thus, it appears that the presence of organic acids does not have a major effect on the reaction rate constants, and as such, these acids are not the

major cause for the observed differences in performance between thick juice and SUC.

Effects of Salts. Thick juice contains significant amounts of salts (Table 1). Both cations and anions are known to affect the reaction rates of GLC and FRC conversions to HMF and LA.[22,23] A systematic study was performed to investigate the influence of the salts on the product profiles using salts with potassium, sodium, calcium, and magnesium as the cations and carbonates, chlorides, and sulfates as the anions. All experiments were performed at 180 °C, 0.5 M initial SUC, and with sulfuric acid (0.01 M) as the catalyst. Because of the differences in the basicity of the anions, the pH of the solutions was not similar; these pH effects are taken into account in the discussion. An overview of the experiments is given in Table 3 (runs 19−22 (carbonates), 23−26 (chloride), and 30−33 (sulfates).

Effects of Carbonate Salts. The initial pH of the four experiments run with carbonate salts (pH 3.7−3.8, runs 10−
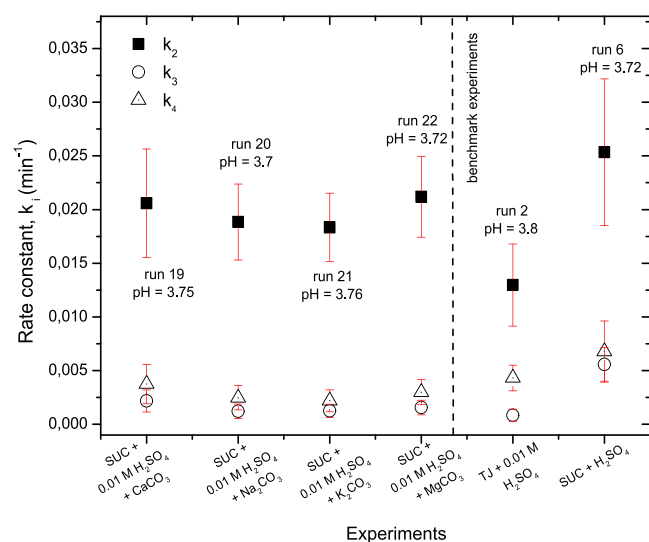
Figure 9. Relevant rate constants for various sucrose (SUC) reactions in the presence of carbonate salts.

22) is higher than for experiments with SUC and sulfuric acid (1.8) and actually similar to that for a thick juice reaction with 0.01 M H_2SO_4 (pH around 3.7−3.8). The concentration−time profiles and the kinetic constants of these experiments are given in Figures 8 and 9, respectively. The concentration−time profiles are all remarkably similar, indicating that the effect of the cations on the rates of reactions within the reaction network is not very pronounced. This was also confirmed by comparing the relevant kinetic constants for HMF (Figure 9), which are similar within the experimental error for these four experiments.

It is of interest to compare the experimental data with the benchmark experiments with SUC and thick juice, which were performed at the same pH value as for the reactions with the carbonate salts. As shown in Figure 9, the k_2 values for the carbonate experiments are slightly more in line with those of SUC, whereas k_3 and k_4 are very similar to those of thick juice. The molar intakes of the salts in the SUC experiments (0.008−0.011 M) are in the range of sulfuric acid (0.01 M). Thus, the carbonate anions are expected to be close to being quantitatively converted to CO_2 and water, and as such, only the cations and sulfate anions are present in the solution. The data imply that these sulfate anions (from sulfuric acid) have an impact on the reaction rates in the network (vide infra) and particularly lower the rate of the reactions 3 and 4 [from HMF to LA (k_3) and to humins (k_4)].

Effect of Chloride Salts. Four experiments (Table 3, runs 23−26) were performed with calcium, sodium, potassium, and magnesium chlorides in the presence of sulfuric acid (0.01 M). The initial pH values of the solutions were between 1.9 and 2.0. The concentration−time profiles of these experiments are given in Figure 10 and the main kinetic constants in Figure 11. As the pH is shown to affect the rates considerably when the pH is below 2, the experimental data are compared with SUC and thick juice experiments at the same pH (1.8−1.9) and not to the benchmark experiments (pH 3.8).

The concentration−time profiles shown in Figure 10 are very similar to the pure SUC hydrolysis reaction (0.01 M H_2SO_4 catalyst at initial pH of 1.8), implying only a minor effect of the addition of chloride salts. This is confirmed by comparing the relevant kinetic constants (Figure 11), which

are similar to those for pure SUC. The only exception is KCl, which shows lower values for particularly k_2 and k_4. It implies that particularly this cation may affect the rate of these reactions, though we will show later that the effect of specifically sulfate anions is by far more pronounced.

Effect of Sulfate Salts. The experiments with carbonate and chloride salts did not reveal any effect of the cations on the rates of the reaction. As such, the full range of cations was not explored and only Na and K sulfate were tested. Experiments were performed at 180 °C, with 0.01 M salt and 0.01 M sulfuric acid concentrations, leading to initial pH values of 1.8 and 1.98 (Table 3, experiments 30 and 33). The concentration−time profiles of these experiments are given in Figure 12, while the main kinetic constants are given in Figure 13. In the latter figure, the kinetic constants for experiments with thick juice and SUC at pH 1.8 (instead of the benchmark) are provided to avoid interference with pH effects.

The experimental data given in Figure 13 reveal that the sulfate anions indeed have a major effect on the rate of the major reactions involving HMF. While the rate constant k_1 remained similar, a noticeable decrease was observed for k_3 and k_4, particularly for k_2. The rate constant k_2 has reduced fourfold when comparing the experiments with pure SUC with those in the presence of sulfate anions. Of relevance is the observation that the actual rate constants are now very close to those found for thick juice, a very good indication that particularly, the presence of sulfate ions in the thick juice causes the major difference in performance for HMF synthesis compared to pure SUC. Of relevance, and in line with the chloride and carbonate experiments, is also the observation that cation effects are absent, except for a small effect of K^+ (vide supra). As such, cation effects are much smaller than sulfate effects and do not play a major role in the reaction rates for the individual reactions.

To probe the effects of the concentration of the sulfate salts, additional experiments were performed with other Na_2SO_4 concentrations. As such, three Na_2SO_4 concentrations were tested (0.01, 0.05, 0.1 M, and 0.5 M SUC and 0.01 M sulfuric acid, Table 3 runs 30−32). The initial pH values for these experiments were dependent on the sulfate concentration and were at 1.8, 2.18, and 2.29, respectively. The concentration−time profiles obtained from these experiments are presented in Figure 14, and relevant kinetic constants are given in Figure 15. The data in the latter figure show that the values of the kinetic constants are dependent on the sulfate concentrations, with higher sulfate concentrations leading to lower values of k_2−k_4. However, this statement is not necessarily true, as also the pH of the solutions is a function of the sulfate concentrations, with higher concentrations leading to higher pH values (from 1.8 at 0.01 M Na_2SO_4 to 2.3 at 0.1 M Na_2SO_4). Though these trends, caused by buffering effects, are relatively small, the rate constants in this pH regime are a function of the pH; see Figure 5 for details.

Discussion. The results given above indicate that the main rate constants for HMF reactions in the reaction network (k_2−k_4) are a function of the pH of the solution, whereas the presence of salts (< 0.01 M) in the form of anions, like carbonates and chlorides as well as cations, like Na^+, K^+, Ca^{2+}, and Mg^{2+}, has no or a small (K^+) effect. The only exception is sulfate ions, which lead to a considerable reduction in the relevant kinetic constants. This remarkable observation may be due to several effects. It may be related to the H_2SO_4/SO_4^{2-} couple, which is a known buffer and will affect the pH
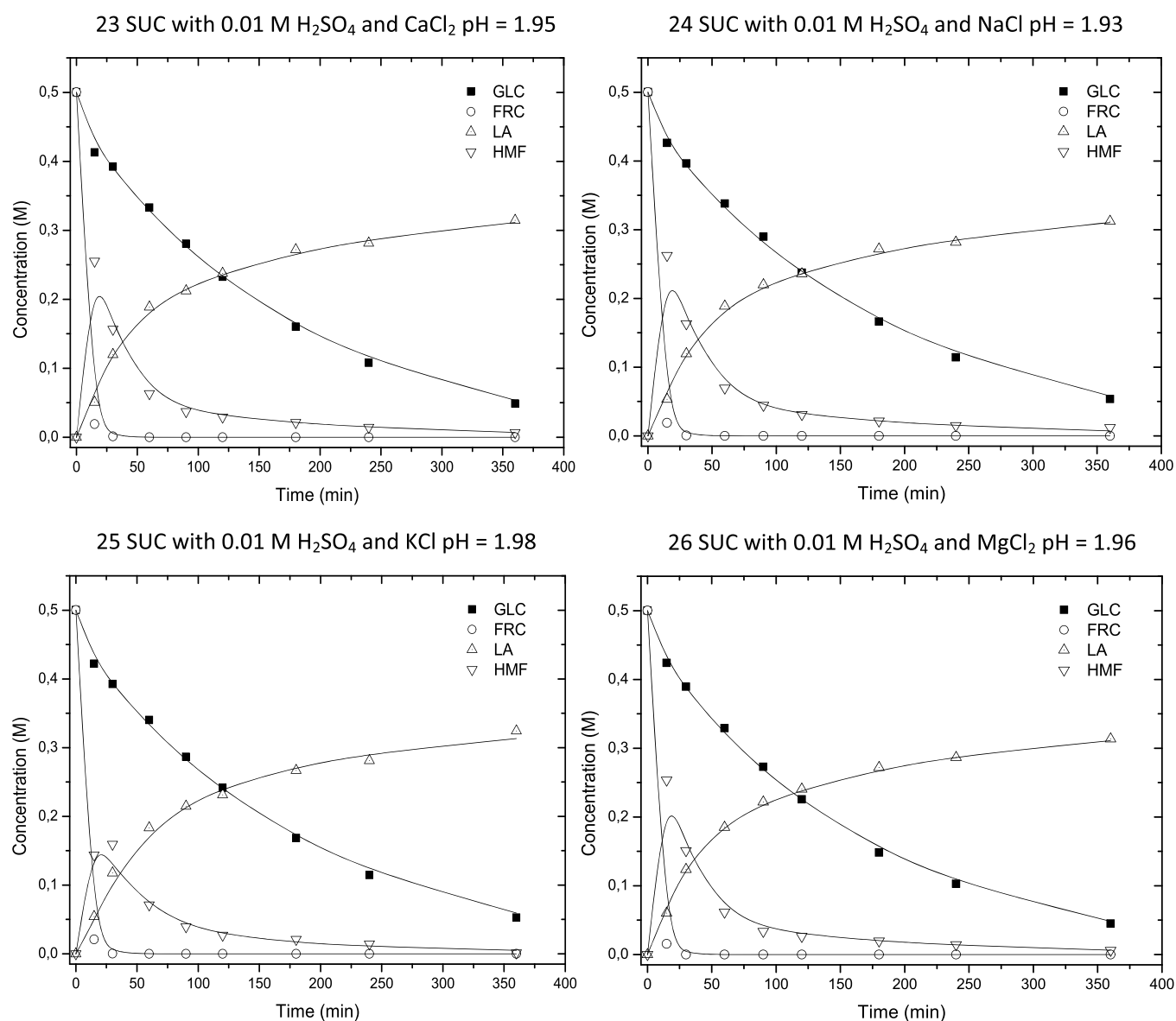
Figure 10. Concentration−time profiles for sucrose (SUC) hydrolysis in the presence of chloride salts. Reaction condition: $C_{SUC(equivalent),0}$ = 0.5 M, 0.01 M H_2SO_4 T = 180 °C. The solid lines represent the model values, while the numbers above the graphs correspond to the run numbers in Table 3.

development during a batch reaction. In the case of reactions with sulfuric acid only, significant amounts of LA and FA are formed (Figure 1), which will affect the pH of the reaction mixture. In the presence of SO_4^{2-}, buffering effects will occur and a more constant pH during the reaction is expected, which likely affects the rates. Another explanation could be a specific involvement of the sulfate anion on certain reactions within the network. As the rate for the relevant reactions involving HMF is reduced in the presence of sulfate anions, intermediates in the reactions may be stabilized by the formation of sulfates[24] because of reactions of the sulfate anion with monoalcohol groups present in the reactants and intermediates.

Additional SUC experiments with HCl as the catalyst in the presence of sulfate anions were performed to determine whether the buffering effect of the H_2SO_4/SO_4^{2-} couple plays a major role. These experiments were carried out at similar conditions as for H_2SO_4 (0.05 M) and in the presence of Na_2SO_4 (0.05 and 0.1 M, Table 3, runs 34 and 35). The

concentration profiles and the modeled kinetic constant of these additional HCl catalyzed reactions are provided in Figures 14 and 15, respectively. The concentration profiles when using HCl as the catalyst are very similar to those obtained with H_2SO_4, and also only minor differences are found for the relevant kinetic constants. Based on these findings, we conclude that buffering effects are less important and that a very specific involvement of sulfate anions on certain reactions in the network is likely the cause of the sulfate anion effect.

The performed kinetic modeling activities also allow for the determination of those conditions where the yield of HMF from SUC is at its maximum and at which batch time this maximum occurs. Details regarding the calculations are given in the Supporting Information, and the results of the calculations are given in Table 3 and Table S2 (Supporting Information). The highest modeled yield was 34%, obtained for SUC using sulfuric acid (0.01 M) in combination with
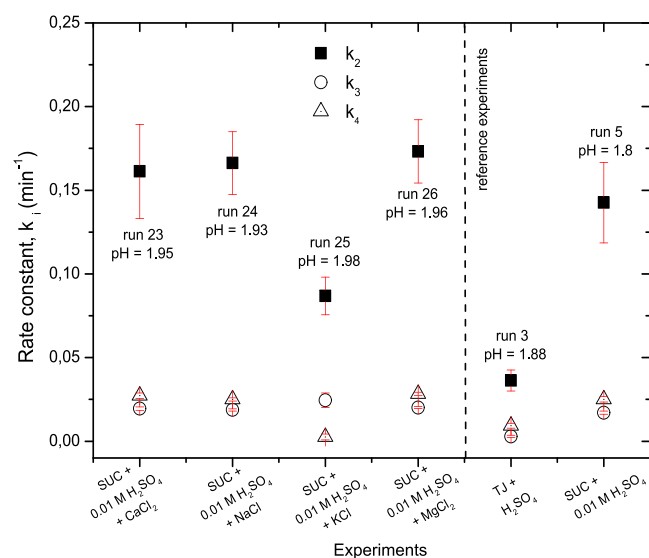
Figure 11. Relevant rate constants for various sucrose (SUC) reactions in the presence of chloride salts.

Figure 13. Rate constants for relevant reactions during SUC hydrolysis in the presence of sulfate salts.

Na_2SO_4 (0.05 M), which is higher than that for an experiment with SUC and sulfuric acid only (0.01 M, 30%). However, the higher yield is obtained at longer batch times (85 min versus 12 min) because of the negative effect of sulfates on the relevant reaction rates (vide supra). This study confirms the existence of differences between thick juice and pure SUC in reactivity for HMF synthesis. This is mainly due to the presence of impurities in the thick juice. It is now evident that neither the organic acids nor the cations in the thick juice are the major cause of these differences, but that it is particularly related to the presence of sulfate anions.

■ CONCLUSIONS

A model study using SUC, either pure or in the presence of impurities known to be present in thick juice (e.g., organic acids and salts), was performed using water as the solvent and sulfuric acid as the catalyst. The experimental data, supported
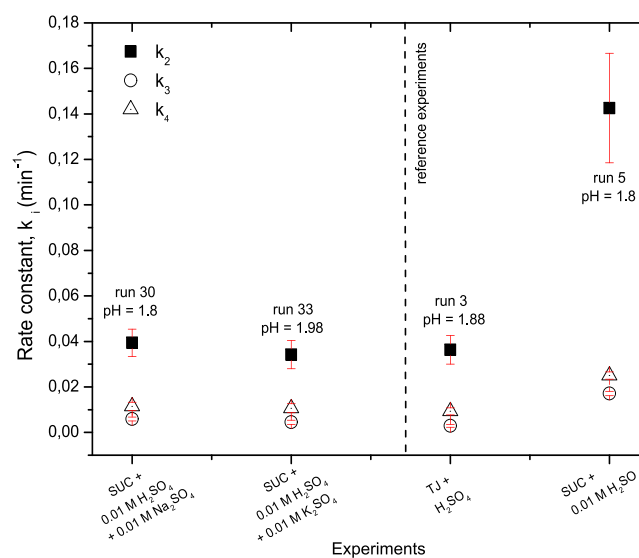
by kinetic modeling, show that the rates of the individual reactions in the network are strongly affected by the pH of the solutions. By carefully considering these pH effects, the effects of organic acids and a range of salts with potassium, sodium, calcium, and magnesium as the cations and carbonates, chlorides, and sulfates as the anions on the individual reaction rates in the network could be assessed. It was shown that particularly the presence of salts with sulfate anions at the level present in thick juice has a positive effect on HMF yields, possibly because of the specific involvement of the sulfate anion on certain reactions within the network. The results imply that the impurities in the thick juice have a positive impact on the conversion of SUC to HMF. As such, it shows that the presence of such impurities in biofeeds does not necessarily have to be detrimental and that the use of crude feedstock can also bring unexpected advantages. It also amplifies our previous suggestion[14] that thick juice is a very
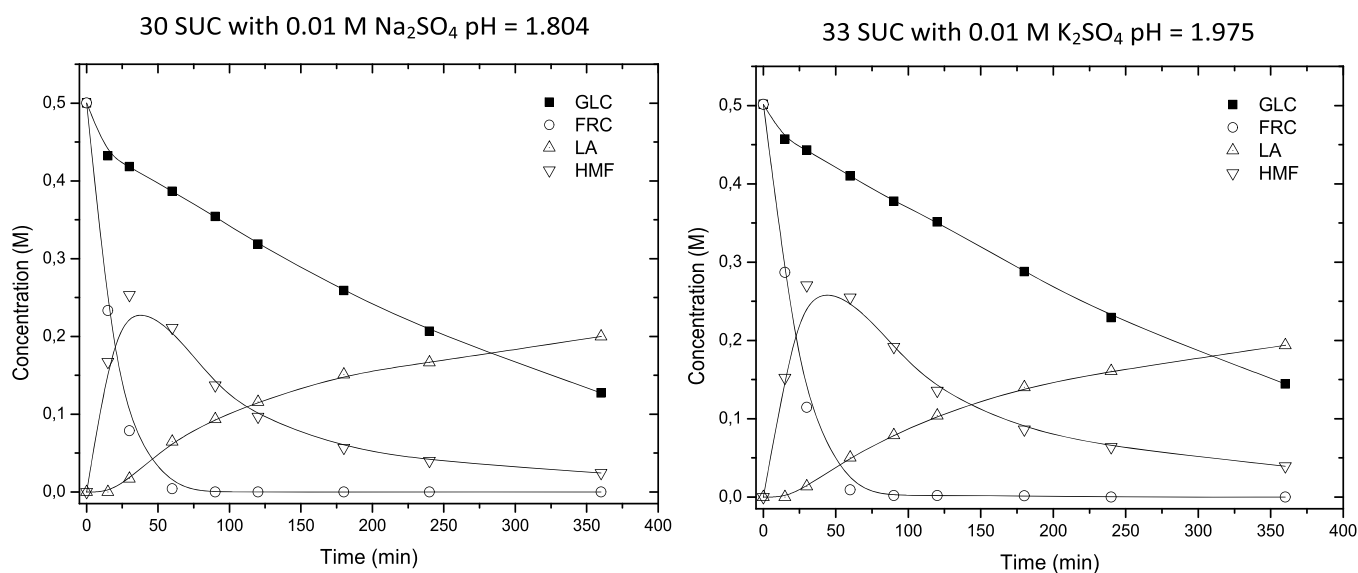

Figure 12. Concentration−time profiles of SUC hydrolysis in the presence of sulfate salts. Reaction conditions: $C_{SUC'0} = 0.5$ M, 0.01 M H_2SO_4 T = 180 °C. Solid lines represent model values. Numbers above the graphs correspond to run numbers given in Table 3.
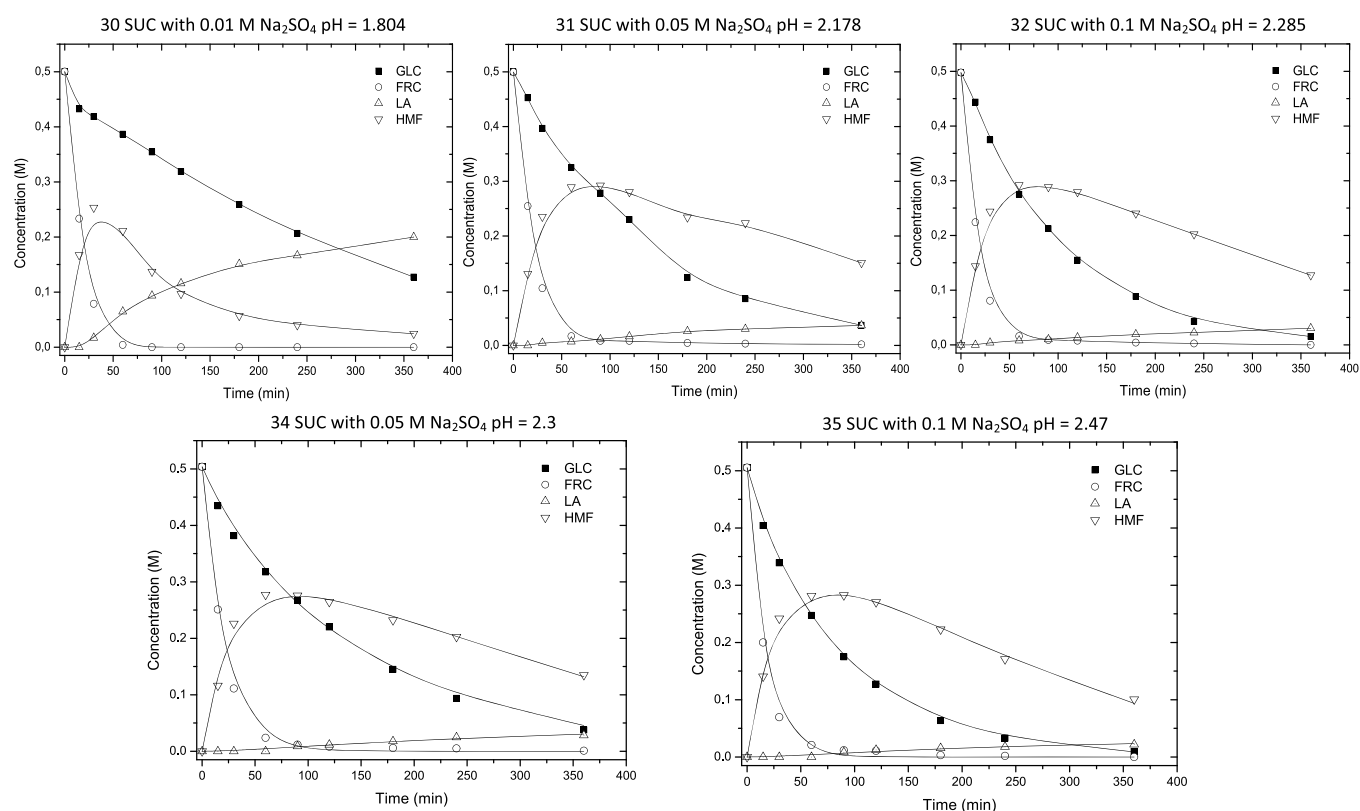
Figure 14. Concentration−time profiles of SUC hydrolysis in the presence of sulfate salts at different concentrations. Reaction conditions: $C_{SUC,0}$ = 0.5 M and 0.01 M H_2SO_4 (for runs 30−32), 0.01 M HCl (for runs 34 and 35) and T = 180 °C. Solid lines represent model values. Numbers above the graphs correspond to run numbers given in Table 3.
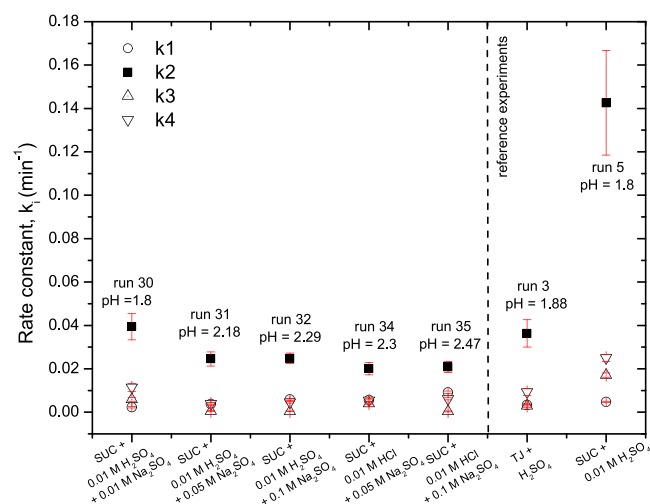

Figure 15. Rate constants for relevant reactions during SUC hydrolysis at different concentrations of Na_2SO_4 and different catalysts (H_2SO_4 for runs 30−32 and HCl for runs 34 and 35).

attractive feedstock for HMF synthesis, as it is expected to be a significantly cheaper feed than refined SUC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c06579.

Description of the determination of the sucrose content in the feed and products; schematic representation of a sugar beet processing unit; visual appearance of reaction mixtures; replicate experiments; concentration profiles for all experiments; a plot of the value of k_2 versus the [H^+]; description of the method to determine the maximum HMF yield from kinetic constants; literature data on the conversion of SUC to HMF, and an overview of all experiments including values of the kinetic constants (PDF).

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Notes

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■ REFERENCES

(1) Mukherjee, A.; Dumont, M.; Raghavan, V. Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities. *Biomass Bioenergy* **2015**, *72*, 143−183.

(2) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484−489.

(3) Román-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982−985.

(4) Kreissl, H. T.; Nakagawa, K.; Peng, Y.; Koito, Y.; Zheng, J.; Tsang, S. C. E. Niobium oxides: correlation of acidity with structure and catalytic performance in sucrose conversion to 5-hydroxymethylfurfural. *J. Catal.* **2016**, *338*, 329−339.

(5) Lange, J.-P.; van der Heide, E.; van Buijtenen, J.; Price, R. Furfural—a promising platform for lignocellulosic biofuels. *ChemSusChem* **2012**, *5*, 150−166.

(6) van Putten, R.-J.; van der Waal, J. C.; De Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de Vries, J. G. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chem. Rev.* **2013**, *113*, 1499−1597.

(7) Jeong, G.-T.; Ra, C. H.; Hong, Y.; Kim, J. K.; Kong, I.; Kim, S.; Park, D. Conversion of red-algae Gracilaria verrucosa to sugars, levulinic acid and 5-hydroxymethylfurfural. *Bioprocess Biosyst. Eng.* **2015**, *38*, 207−217.

(8) Teong, S. P.; Yi, G.; Zhang, Y. Hydroxymethylfurfural production from bioresources: past, present and future. *Green Chem.* **2014**, *16*, 2015−2026.

(9) Tan-Soetedjo, J. N.; van de Bovenkamp, H. H.; Abdilla, R. M.; Rasrendra, C. B.; van Ginkel, J.; Heeres, H. J. Experimental and Kinetic Modeling Studies on the Conversion of Sucrose to Levulinic Acid and 5-Hydroxymethylfurfural using Sulfuric Acid in Water. *Ind. Eng. Chem. Res.* **2017**, 13228−13239.

(10) Wang, T.; Nolte, M. W.; Shanks, B. H. Catalytic dehydration of C 6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green Chem.* **2014**, *16*, 548−572.

(11) Feather, M. S.; Harris, J. F. On the mechanism of conversion of hexoses into 5-(hydroxymethyl)-2-furaldehyde and metasaccharinic acid. *Carbohydr. Res.* **1970**, *15*, 304−309.

(12) Harris, D. W.; Feather, M. S. Evidence for a C-2→ C-1 intramolecular hydrogen-transfer during the acid-catalyzed isomerization of D-glucose to D-fructose ag. *Carbohydr. Res.* **1973**, *30*, 359−365.

(13) Harris, D. W.; Feather, M. S. Intramolecular carbon-2. far. carbon-1 hydrogen transfer reactions during the conversion of aldoses to 2-furaldehydes. *J. Org. Chem.* **1974**, *39*, 724−725.

(14) Abdilla-Santes, R. M.; Guo, W.; Bruijnincx, P. C. A.; Yue, J.; Deuss, P. J.; Heeres, H. J. High yield 5-hydroxymethylfurfural synthesis from crude sugar beet juice in a biphasic microreactor. *ChemSusChem* **2019**, *12*, 4304−4312.

(15) Tan, L.; Sun, Z.; Okamoto, S.; Takaki, M.; Tang, Y.; Morimura, S.; Kida, K. Production of ethanol from raw juice and thick juice of sugar beet by continuous ethanol fermentation with flocculating yeast strain KF-7. *Biomass Bioenergy* **2015**, *81*, 265−272.

(16) van Zandvoort, I.; *Towards the valorization of humin by-products: characterization, solubilization and catalysis* (Doctoral dissertation), Utrecht University (2015).

(17) Girisuta, B.; Janssen, L. P. B. M.; Heeres, H. J. Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. *Chem. Eng. Res. Des.* **2006**, *84*, 339−349.

(18) Pilath, H. M.; Nimlos, M. R.; Mittal, A.; Himmel, M. E.; Johnson, D. K. Glucose reversion reaction kinetics. *J. Agric. Food Chem.* **2010**, *58*, 6131−6140.

(19) Pedersen, A. T.; Ringborg, R.; Grotkjær, T.; Pedersen, S.; Woodley, J. M. Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose−fructose mixtures. *Chem. Eng. J.* **2015**, *273*, 455−464.

(20) Kuster, B. F. M.; van der Baan, H. S. The influence of the initial and catalyst concentrations on the dehydration of D-fructose. *Carbohydr. Res.* **1977**, *54*, 165−176.

(21) Zhang, X.; Hewetson, B. B.; Mosier, N. S. Kinetics of maleic acid and aluminum chloride catalyzed dehydration and degradation of glucose. *Energy Fuels* **2015**, *29*, 2387−2393.

(22) Wu, X.; Fu, J.; Lu, X. Hydrothermal decomposition of glucose and fructose with inorganic and organic potassium salts. *Bioresour. Technol.* **2012**, *119*, 48−54.

(23) García-Sancho, C.; Fúnez-Núñez, I.; Moreno-Tost, R.; Santamaría-González, J.; Pérez-Inestrosa, E.; Fierro, J. L. P.; Maireles-Torres, P. Beneficial effects of calcium chloride on glucose dehydration to 5-hydroxymethylfurfural in the presence of alumina as catalyst. *Appl. Catal. B.* **2017**, *206*, 617−625.

(24) Al-Horani, R. A.; Desai, U. R. Chemical Sulfation of Small Molecules-Advances and Challenges. *Tetrahedron* **2010**, *66*, 2907−2918.