Hydrolysis of Sucrose over Sulfonic Acid Resins
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Sucrose hydrolysis on acidic ion-exchange resins is a long-established process in the sugar industry, but the formation of side products is less understood. A resin typically used in the industrial process (C124SH, Purolite) was investigated in a broad range of sucrose concentration (7 to 75 % w/w) and temperatures from 25 to 80 °C. Fructose is converted to 5-hydroxymethylfurfural (HMF) due to a 1/2 order reaction. This is explained by the formation of a fructosyl disaccharide (monoanhydride) as an intermediate decomposing to HMF and fructose. Difructose dianhydrides (DFAs) are separately formed as prevailing by-products. The color of the product mixture is correlated to HMF and found to be reduced by size exclusion inside the resins. Diffusional limitations of the total reaction are investigated by comparison of the entire resin bead with its size-reduced forms obtained by milling. Without diffusion limitation the catalytic activity increases with the sugar concentration while the diffusion control leads to a maximal activity around 40 % w/w sugar. Diffusion coefficients of sucrose are calculated.

1. Introduction

The worldwide isolation of sucrose from sugar beet and sugar cane amounts to about 180·10^6 t a^-1 and maintains the first position among all chemically pure substances.[1] About 8 % of the sugar is estimated to be hydrolyzed to a mixture of fructose, glucose, and residual sucrose. A mixture of one part of each component is as sweet as pure sucrose but bears advantages in food technology, mainly because of its high solubility.[2] Furthermore, the complete sugar hydrolysis can substitute the component is as sweet as pure sucrose but bears advantages in food technology, mainly because of its high solubility.[3] The complete sugar hydrolysis can substitute the side products is less understood. A resin typically used in the industrial process (C124SH, Purolite) was investigated in a broad range of sucrose concentration (7 to 75 % w/w) and temperatures from 25 to 80 °C. Fructose is converted to 5-hydroxymethylfurfural (HMF) due to a 1/2 order reaction. This is explained by the formation of a fructosyl disaccharide (monoanhydride) as an intermediate decomposing to HMF and fructose. Difructose dianhydrides (DFAs) are separately formed as prevailing by-products. The color of the product mixture is correlated to HMF and found to be reduced by size exclusion inside the resins. Diffusional limitations of the total reaction are investigated by comparison of the entire resin bead with its size-reduced forms obtained by milling. Without diffusion limitation the catalytic activity increases with the sugar concentration while the diffusion control leads to a maximal activity around 40 % w/w sugar. Diffusion coefficients of sucrose are calculated.

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The acid splitting of sucrose as first-order reaction occurs at the fructosyl oxygen[5,6] and only depends slightly on the nature of the acid anion.[7] Also in strong acid aqueous[8] and mixed aqueous solutions[9,10] the proton activity is related to the acidity as measured by the protonation of amine indicators (Hammett acidity function). At fixed pH the change of the aqueous medium by the sucrose itself does not have an influence on the ideal kinetics which is proportional to the concentration of sucrose and water up to a mass fraction of 70 %.[11] The activation energy amounts to 107 kJ mol^-1 K^-1.[12,13,14]

The first example of sucrose hydrolysis on an acid ion-exchange resin has been published in 1949[15] It was found that the activity can be enhanced by milling the resin which clearly indicates the existence of a diffusion limitation. Further fundamental knowledge has been published by Kunin during his work at the former Rohm and Haas Company[16] The catalytic activity of the sulfonic acid polystyrene-divinylbenzene resins in a 2.5 % w/w sucrose solution decreases with increasing particle size and is slowed down by a factor of 300 when the degree of crosslinking is increased from 1 % to 20 %. The diffusion limitation decreases the apparent activation energy[16] Later work verified these results also for higher sucrose concentrations up to 45 %.[17,18] The observed reaction rate not only results from the concentration gradient of sucrose inside the resin but also reflects the equilibrium concentration which is lower inside than outside the resin[19] the isotherm following an anti-Langmuir behavior.[20] Siegers and Martinola[21] investigated different sulfonic acid resin differing in the content of divinylbenzene (dvb) with pure gel-type (4–8 % dvb) and mixed gel-macro structure (5–18 % dvb) and found that the 4 % gel and the 5 % gel-macro resin had the best performance in the sucrose hydrolysis under industrial relevant conditions with sucrose concentrations around 50 % at 40 °C and 99 % conversion.

A matter of particular interest is the formation of 5-hydroxymethylfurfural (HMF) which arises from fructose by acid catalyzed dehydration. Since a health risk is discussed for HMF in nutrition[22] and because HMF is correlated with the formation of color (extinction at 420 nm),[23] the concentration of that compound must be reduced. Its adsorption on activated carbon[24] or hydrophobic resins[25,26] is possible, and it can also react as an aldehyde with immobilized amino groups.[27] However, in practice, the formation of colored side products is limited by restricting the temperature of the hydrolysis in ion-exchange resins to a maximum of 40 °C. The industrial reaction is thus performed on a fixed bed of sulfonic acid resin at that

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temperature and with a sucrose concentration between 50 and 60\%.[36]

Besides the formation of HMF, a further consecutive reaction exists which can be described by the concept of reversion products. These are isomers of sucrose formed by the back-reaction of glucose and fructose\(^{28}\) and higher oligomers of mainly unknown molecular structure.\(^{35,36}\) In general, the concentration of these products is expected and found to increase with the total sugar concentration.\(^{30}\) As the product analysis in industrial hydrolysis plants systematically yields some percent less fructose than glucose, special reaction pathways for fructose were assumed.\(^{31}\) Pure concentrated fructose solutions are transformed to difructose anhydrides (DFAs) in the presence of sulfonic acid resins.\(^{32}\) Those isomeric spiro compounds are formed by cyclization of two fructose molecules releasing two water molecules. They have been detected in industrial invert sugar liquid.\(^{33}\) At last, the reaction of the DFAs with either glucose or fructose to glycosyl-DFA is also conceivable.\(^{34}\)

In view of this background and in order to obtain a deeper understanding of the side product formation, we present here a broad kinetic analysis of sucrose hydrolysis over sulfonic acidic resins including the formation of HMF, color, and reversion products. For that purpose the influence of resin morphology is not discussed here and planned to be presented in another contribution. Hence, the present study is mainly restricted to a 4\% crosslinked gel-type resin which is recommended for industrial sucrose hydrolysis by most resin producers.

**Experimental Section**

**Materials**

Samples of industrial sulfonic acid resins were obtained from Lanxess AG (S2328), Finex OY/Johnson Matthey (CS16C), and Purolite (C1245H). Particle size reduction was achieved by ball-milling. Sucrose (refined, extra white EU quality 1) was provided by Nordzucker AG (Germany), and fructose, glucose, and sorbitol were purchased from VWR in analytical grade (\(>99.5\%\). Food grade industrial invert sugar syrups 72.7/66 and 72.7/100 with dry matter content of 72.7\% w/w and hydrolysis degrees of 67 or 99\% resp. were provided by Nordzucker AG.

**Preconditioning of the resins**

To reduce the release of acid substances into the liquid reaction mixture the resins were pretreated as follows: S2328 was eluted in a column with 5 bed volumes distilled water within a total contact time of 2 days, and afterwards with 5 bed volumes methanol within a total contact time of 3 days. Finally, the resin was eluted with 2 bed volumes water, 2 bed volumes of 1 M HCl, with water, and finally with extra pure water (\(<0.2 \mu S\)) until the pH was 6 for longer than 24 h. After that the resins were surface-dried by water jet vacuum and stored. The C1245H resin was treated in a similar manner but with enhanced temperature and by additional boiling in isopropanol.

**Dry substance**

The part of water absorbed by the resins was determined by an automatic rapid dryer (Mettler Toledo HG53 halogen analyzer). The program for the analysis of tightly bound water (method 5) was chosen.

**Ion-exchange capacity**

A known mass of resin is placed in a column. After washing with distilled water the resin is eluted with a 40 g L\(^{-1}\) solution of Na\(_2\)SO\(_4\) and the acid eluate is titrated with 0.1 M NaOH against pH 7.0.

**Determination of swelling**

The degree of swelling was determined by placing 1 g of fresh dried resin \(m_0\) (24 h, 70 °C, \(<1\) mbar)\(^{35}\) in a mass \(m\) around 10 g of an aqueous solution of 0.2 g L\(^{-1}\) blue dextran (MW = 2 \(\times 10^6\) g mol\(^{-1}\), Sigma). The suspension was gently shaken for 1 h and then stored under quiescence over night. The liquid was sucked without filtration by a syringe and analyzed in a two beam UV-VIS spectrophotometer (JASCO 530). The difference between the extinction at 614 nm and 800 nm was used for the determination of the dextran, 800 nm being a measure of color released by the resin. The swelling is then defined as the mass of the dextran-free liquid per resin dry mass according to Equation (1)

\[
q = \frac{(1 - c_0/c) \ m_i}{m_{os}}
\]  

with \(c_0\) being the concentration of dextran before and \(c\) after the contact with the resin.

**Resin size**

Particle size and size distribution of the resins suspended in water was analyzed by laser diffraction with Helios device of Sympatec GmbH (Germany).

**Sucrose hydrolysis test reaction**

Aqueous solutions of 300 g sucrose or mixtures of sucrose with other sugars were prepared in a weight fraction up to 60\%. Just to be sure that inorganic impurities can be neglected, the solution was slightly stirred with 1 g wet cation exchange resin in the H\(^{+}\)-form (S2568, Lanxess) and the same amount of an anion exchange resin (S6368A, Lanxess) for 15 h at 8 °C in a fridge and the resins were then removed by a sieve. To obtain higher concentrated solutions the liquids were treated in a rotating evaporator at 40 to 50 °C.

The hydrolysis reaction was performed in a thermostatted stirred vessel and the reaction was started by the addition of the wet resin. Samples were obtained by pressing them through a 0.22 \(\mu m\) teflon filter. After appropriate dilution they were analyzed by HPLC (Agilent Series 1100) on a diol-functionalized silica column (LiChrosorb Diol, inner diameter 4 mm, length 250 mm, Merck-Millipore) with a mixture of 85 \% v/v acetonitrile and 15 \% v/v water at 25 °C.\(^{35}\) The sugars were detected by RI and HMF by UV at 280 nm. HMF appears in front of the system peak. That unusual analysis was verified by means of a C18 column with 95\% water and 5\% acetonitrile as eluent.\(^{37}\)
Color formation

To reduce the release of color forming products from the resin compared to those from sugars, the conditioned resin (S2328) was additionally purified by Soxhlet extraction with methanol for 3 days. Extinction coefficients were measured between 300 and 600 nm with a two-beam UV-VIS spectrophotometer (JASCO UV-VIS 530). Color is defined by extinction at 420 nm according to the recommendation of ICUMSA (International Commission for Uniform Methods of Sugar Analysis).

Reversion products

The sugars formed by reversion reaction are assumed to be non-fermentable by yeast. With respect to the work of Sanz et al.\textsuperscript{[32]} the samples from the hydrolysis reaction were diluted to a sugar content of about 10%. To 10 g of that samples 0.5 g baker yeast was added and the only weakly closed plastic vessels (release of CO\textsubscript{2}) were stored at 38 °C for 3 days. After that the samples were centrifuged and the supernatant liquid was stored in a freezer at −20 °C. The thawed samples were two times pressed through a 0.22 mm-telfon filter and than analyzed without further dilution by HPLC as described above in the diol column with 85% acetonitrile 0.22 μm pyridine. After the slow addition of 300 μL hexamethyldisilazane and 150 μL chlorotrimethylsilane the vessel was closed and heated to 60 °C for 15 min. After cooling 1 mL of a 10 g L\textsuperscript{-1} solution of heptadecanoic acid methyl ester in hexane was added as internal standard. The white precipitation is centrifuged and the supernatant liquid was stored in a freezer at −30 °C for 3 days. After that the samples were freeze-dried and than analyzed without further dilution by GC-MS. The mass loss accounts for 4 to 5 %.

2. Results and Discussion

2.1. Characterization of the resins

A main characteristic of polymeric ion-exchangers is their ability to swell in water. An often-applied easy method consists of centrifugation which is accurate when the liquid adsorbed on the bead surface can be neglected.\textsuperscript{[41]} Here, as an alternative new method the swelling is measured by contact of the dried resin with a solution of blue dextran. Due to its high molecular weight of $M_w = 2 \times 10^6$ g mol\textsuperscript{-1} it can be assumed to be excluded from the resin sphere. The method yields the mass of water per dry resin $q_w$.

Respective data for the three industrial sulfonic acid resins, used in this work, are compiled in Table 1. The specific volumes are accessible by the relationship\textsuperscript{[42]} (Eq. (2))

$$v_r = v_{polym} + q_w/\rho_w$$

with $\rho_w$ being the density of pure water and $v_{polym}$ an apparent additive contribution of the polymer skeleton volume. $v_{polym}$ is found to be 0.63 cm\textsuperscript{3}g\textsuperscript{-1} for typical mono-sulfonated gel-type styrene-dvb resins in the H\textsuperscript{+} form independent on the degree of crosslinking.\textsuperscript{[42]}

Besides the specific volume, the average size of the pores is of interest, too. A rather simple presentation of the sulfonated polystyrene-dvb network is a 3-dimensional mesh which is stretched to cubes. Regarding a 4% crosslinked resin and neglecting the statistical nature of crosslinking, each cube has 12 edges, each composed of 24 sulfonated styrene (Mw = 184) plus one dvb (Mw = 130). Due to conformational forces the network is contracted. The cubes deform but deformations cancel by those on the adjacent cubes. At the equilibrium stage a volume of 3.00 cm\textsuperscript{3}g\textsuperscript{-1} is reached. Then, each “soft elementary

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Table 1. Characterization of sulfonic acid resins C124SH (Purolite), CS16C (Finex) and S2328 (Lanxess) by the degree of crosslinking with dvb, by the average pore diameter $d_p$, by the median size $d_m$, by the specific volume $v_i$, by swelling in water $q_w$, by ion-exchange capacity $n_{ex}$, and by the local proton concentration $n_{h+}/q_w$.

|      | dvb (%) | $d_p$ [nm] | $d_m$ [nm] | $v_i$ [cm$^3$g$^{-1}$] | $q_w$ [g g$^{-1}$] | $n_{ex}$ [nmol g$^{-1}$] | $n_{h+}/q_w$ [nmol g$^{-1}$] |
|------|---------|------------|------------|------------------------|-------------------|-------------------------|--------------------------------|
| C124SH | 4       | 8.04       | 0.700      | 3.00                   | 2.372             | 5.01                    | 2.11                          |
|       |         |            | 0.200      | 0.063                  |                   |                         |                               |
|       |         |            |            |                        |                   |                         |                               |
| CS16C | 8       | 5.30       | 0.320      | 1.73                   | 1.104             | 5.01                    | 4.54                          |
|       |         |            | 0.220      | 0.086                  |                   |                         |                               |
|       |         |            |            |                        |                   |                         |                               |
| S2328 | 5       | 7.38       | 0.846      | 2.91                   | 2.284             | 4.78                    | 2.09                          |
"cell" occupies an average volume of 272 nm$^3$. A sphere with the same volume has a diameter of 8.0 nm. Hence, the average pore radius, based on the dvb content, is given in a general form by Equation (3)

$$r_p = \frac{3 \times 12 \cdot n}{4 \pi \cdot (1 - x) \cdot 184 + 130 \times N_d}$$

(3)

The same consideration is possible for the 5% crosslinked resin S2328 (cf. Table 1). However, S2328 is a macroporous resin where the condition of an isotropic distribution of cross-links is not valid. The internal water-filled volume is given as a fraction of somewhat smaller "gel-type" pores and another with larger macropores. These macropores can also be present in the dry state without the swelling pressure and, therefore, it is possible to detect them by nitrogen sorption at 77 K and by Hg-intrusion.$^{[43]}$ However, macroporous resins with low degree of crosslinking have viscoelastic flexible pore walls which can deform during the drying process.$^{[44]}$ Thus, a dry macroporous resin with 8% dvb (Amberlyst 39) is reported to have a measurable surface near zero.$^{[45]}$ Therefore, respective data for S2328 (5% dvb) are omitted in this work.

### 2.2. Homogeneous and quasi-homogeneous catalysis

In the following kinetic analysis, the sugar concentration varies from 5 to 75% w/w. Therefore, sucrose not only acts as reactant but also by changing the solvent properties. Hence, in that special case the reaction rate constant must depend on the concentration of all sugars present in the reaction mixture. For example, a 70% w/w sucrose solution has a density of 1.348 g L$^{-1}$ and a viscosity of 482 mPa s at 20°C compared to the corresponding values of 1.00 g L$^{-1}$ and 1.00 mPa s for pure water.$^{[46]}$ Self-diffusion coefficients of sucrose$^{[47]}$ and remaining water molecules$^{[48]}$ are changed, too. During the reaction 1 mol sucrose is split to 1 mol glucose plus 1 mol fructose under the consumption of 1 mol water. Complete conversion yields then only 5% more mass of total sugar which means that the conversion of a 70% w/w sucrose solution ends at 73.5% w/w invert sugar solution where the density is increased by 1% to 1.362 g L$^{-1}$ but the viscosity is decreased by 25% to 363.7 mPa s at 20°C.$^{[49]}$ The kinetic study, presented hereinafter, considers the influence by the total sugar concentration being nearly the same as the initial sucrose concentration. The influence of the sugar composition is neglected and only interpreted in some cases by the observation of trends.

The overall reaction kinetics is determined by the mass transport inside the resin beads having a diameter of 0.3 and 0.8 mm. To study the micro-kinetics inside smaller volume fractions of the beads, the resin C124SH (4% dvb) was milled to a mean particle size of 63 μm. It is assumed that such a resin has no diffusional limitation.

In a diluted sucrose solution with HCl as catalyst the reaction kinetics is given by a rate law using the concentration of sucrose [S] and the proton activity $a^+$. [Eq. (4)]

$$a^+ = f^+ [H^+]$$

(4)

When the sugar concentration increases, the concentration of water [H$_2$O] has to be considered, too. Hence, the rate law of the reaction is given by Equation (5)$^{[11]}$

$$-d[S]/dt = k^+ [H^+] \cdot [S] \cdot [H_2O]$$

(5)

where [H$_2$O] is linked to the solution density $\rho$ by Equation (6)

$$[H_2O] = \rho - [S]$$

(6)

When the acid concentration [H$^+$] is held constant but the sugar concentration is increased, two contrary effects have to be considered: First, less water must reduce the reaction rate because it is proportional to [H$_2$O], secondly the proton activity coefficient increases. If we comprise these two effects by [Eq. (7)]

$$k^+ = k f^+ [H_2O]$$

(7)

the reaction rate can be written as Equation (8)

$$-d[S]/dt = k^+ \cdot [H^+] \cdot [S]$$

(8)

An early study of 1922$^{[49]}$ has documented a linear increase of the reaction rate constant $k^+$ with the volumetric sucrose concentration at 25 and 35°C (see Figure A1 of the SI). That investigation refers to an acidity caused by a 0.1 mol L$^{-1}$ HCl in an aqueous sucrose solution up to 700 g L$^{-1}$. Since the difference of the slope between 25 and 35°C is negligible, the same increase can be assumed also for 60°C based on literature data for dilute sucrose.$^{[10]}$ The dependence of the rate constant with the sugar concentration at 60°C is shown in Figure 1. The corresponding red line is as follows [Eq. (9)]:

$$k^+_{HCl} = a_1 + a_2 \cdot [S]$$

(9)

with $a_1 = 0.685$ L mol$^{-1}$ min$^{-1}$ and $a_2 = 9.05 \times 10^{-4}$ L$^2$ g$^{-1}$ mol$^{-1}$ min$^{-1}$. The definition of the rate constant $k^+$, given in Equation (8), can be applied to the resin-catalyzed reaction as well. The concentration of acid groups [H$^+$] is then conceived to be related to the total reaction volume, differing to the true acid solution by local higher concentrations inside the resin volume. As in the cited experiment with HCl, the catalysis with the milled C124SH resin was performed at concentrations per reactor volume around [H$^+$] = 0.1 mol L$^{-1}$. The rate constant $k^+$ inside the resin is significantly lower, but shows a similar trend. When the $k^+$ values of the resin are plotted against those of HCl, it is evident that a positively bent curve starting in the origin correlates both rate constants with each other. (see supporting information Figure A2) [Eq. (10)].
By combining Equations (9) and (10), Equation (11) is obtained:

\[
k^r = 0.290 k^\text{HCl} + 0.222 (k^\text{HCl})^2
\]  

By combining Equations (9) and (10), Equation (11) is obtained:

\[
k^r = 0.303 + 5.37 \times 10^{-4} [S] + 1.81 \times 10^{-7} [S]^2
\]

\[
\text{(in L mol}^{-1}\text{min}^{-1})
\]

This is the blue line of Figure 1 describing the experimental trend of the resin-catalyzed reaction. Due to the concept of quasi-homogeneous catalysis\[51,52\] the main difference between the catalysis with HCl and the resin is the differing sugar concentration inside \([S_r]\) and outside \([S]\). That distribution equilibrium is either described by an equation \[Eq (12)\] of the type\[50,53\]

\[
[S_r] = b_1 [S] + b_2 [S]^2,
\]

by a Freundlich,\[54\] or by an isotherm coined either Anti-Langmuir\[55\] or truncated D Dubinin-Serpinsky.\[56\] The concave isotherm shape can be explained by a significant reduction of the thermodynamic carbohydrate activity at low concentration\[57\] or simply by the high affinity of water towards the ionic sulfonic acid groups. During the present experiments, sucrose is converted to fructose and glucose. Hence a multicomponent system has to be considered. However, due to the addition of one molecule of water to one sucrose molecule, the total carbohydrate mass is only slightly increased by 5%. When the multicomponent adsorption mainly results from the competition with water, the interaction between the different sugars (negative or positive cooperative effects\[58\]) can be neglected. In the following, the resin-catalyzed sucrose hydrolysis is simply compared with literature data concerning the equilibrium of pure sucrose distribution between the aqueous and the resin phase. Only the degree of resin crosslinking (4% dvb) and the temperature (60 °C) are the same while the counter-ion is catalytically inactive Na\(^+\). Such a system is reported to obey Equation (12) with \(b_1 = 0.26\) and \(b_2 = 2.77 \times 10^{-4}\). Changing the ionic form from Na\(^+\) to H\(^+\) is expected to cause a further reduction of \([S_r]\) by 9% \((b_1 = 0.21\) and \(b_2 = 2.52 \times 10^{-4}\)). With the distribution coefficient \[Eq. (13)\]

\[
\lambda = b_1 + b_2 [S]
\]

one obtains for the expected rate constant of the resin \[Eq. (14)\]

\[
k^r = \lambda k^\text{HCl}
\]

shown as black line in Figure 1. The gap to the experimental course (blue) is obvious.

That difference should be ascribed to the nature of acid groups. Homogeneous sucrose hydrolysis was not only investigated with HCl but also with soluble polystyrene sulfonic acid as catalyst.\[60\] The activity of the polymeric acid measured at 25
and 70 °C is only 71 % of that of HCl of the same concentration (compare Table A2 of the SI) and results in the green curve in Figure 1. The gap toward the experiment is enlarged: The experimental rate constant at the boundary value of [S]—0 is 2.6 times greater than the predicted one.

The remaining difference can be explained by a concentration effect. Indeed, the formal proton concentration per reaction volume is independent of the distribution of acid sites, either concentrated in spread resin beads or completely homogeneous throughout the reaction volume, but the much higher local concentration inside the swollen resin causes a higher activity coefficient $f^+$ of the sulfonic acid groups. According to Table 1 the molality of acid in the swelling water is given by $n_{H^+}/q_w = 2.11 \text{ mol kg}^{-1}$ which is much more than the formal acid concentration per reaction volume ranging from 0.015 to 0.020 mol L$^{-1}$ depending on the respective resin weight. During HCl catalysis at lower temperature the rate constant $k^+$ considerably increases above a molality of 0.5 mol kg$^{-1}$. The effect must also be present at 60 °C where the reaction rate is too high to be measured. Assuming the effect is independent on temperature, Figure 2 was constructed for 60 °C based on literature data.$^{[61,62]}$ The enlargement of the resin activity by the factor of 2.6 at $n_{H^+}/q_w = 2.11 \text{ mol kg}^{-1}$ water follows the trend of increasing activity coefficient.

2.3. Diffusional resistance

Since from now on, a comparison with results from homogeneous catalysis is not needed, the use of $k^+$ as reaction rate constant is given up, and a rate constant related to the catalyst volume is used as [Eq. (15)]

$$k_v = k^+ \frac{[H^+]}{m_{H^+}} \frac{V}{m_r v_r} \quad (15)$$

Here $V$ is the reaction volume, $m_r$ the catalyst dry mass and $v_r$ the specific resin volume as defined by Equation (2) via the dextran exclusion method. While the milled resin has been discussed so far because the reaction rate is assumed not to be limited by intraparticle diffusion, now technically important resin beads are considered.

Figure 3 shows the influence of particle (bead) size $d_r$ on the observed reaction rate constant. Its idealized course is modeled by non-linear regression for 3 different particle sizes according to the Thiele concept as [Eq. (16)]

$$k_v = k_{v, o} \frac{3}{\Phi} \left( \frac{1}{\tanh \Phi} - \frac{1}{\Phi} \right) \quad (16)$$

Here $k_{v,o}$ is the rate constant of the true intrinsic reaction rate (independent on diffusion limitations) and $\Phi$ is the Thiele modulus [Eq. (17)]

$$\Phi = \frac{d_r}{2} \sqrt{\frac{k_{v,o} \lambda}{D_r}} \quad (17)$$

where $\lambda$ is the distribution coefficient between sucrose at the resin surface and inside the resin bead. The regression analysis results in $k_{v,o}$ and the effective diffusion coefficient $D_r$. As expected, the true rate constant is only somewhat higher than that obtained with the milled resin. With respect to the applied 40 % w/w (460 g L$^{-1}$)$^{[46]}$ sucrose solution the value of $\lambda$ is calculated to be 0.33 according to Equation (13). The mean concentration of sucrose inside the resin is then 13 % w/w. A
bulk solution of that concentration is characterized by a self-diffusion coefficient of $9.7 \times 10^{-10}$ m$^2$s$^{-1}$ at 60°C, while the diffusion coefficient inside the resin beads is determined by Equations (16) and (17) to be $1.2 \times 10^{-11}$ m$^2$s$^{-1}$. The reduction by the factor of 0.012 is firstly due to the free volume concept and secondly a consequence of steric hindering. The self-diffusion of the small water molecules inside the resin is available in the literature: For the water loading of the present resin being $q_w = 2.73$ (Table 1), the diffusion coefficient is calculated to be reduced by a factor of only 0.56 compared to neat water. When the volume of the soft pores of the C124SH resin is assumed to be 272 nm$^3$ (see Section 3.1) it contains 9000 water molecules, but only 100 sucrose molecules, based on a molecular volume of 0.341–0.344 nm$^3$ and a 13% sucrose solution. One can imagine that interactions of the sugar with the polymer coils may be significant. Thus, the value of $1.2 \times 10^{-11}$ m$^2$s$^{-1}$ is comparable with the diffusion coefficient of sucrose during chromatographic separation estimated to be $6.0 \times 10^{-11}$ m$^2$s$^{-1}$ at 60°C for a 4.8% crosslinked resin. Self-diffusion measurements of sucrose in ion-exchange beads are not available.

For comparison the same investigation with a 8% dvb resin is presented in Figure 3, too. Here, the pore volume is only 67 nm$^3$, and under the prerequisite that the distribution coefficient is around 0.08, that volume provides space for only about 6 sucrose molecules. The curve fitting due to Equations (16) and (17) yields an effective diffusion coefficient of only $4.2 \times 10^{-13}$ m$^2$s$^{-1}$.

The influence of the sucrose concentration on the catalytic activity of the milled C124SH resin has already been discussed and presented in Figure 1. It is interesting to know the difference towards the catalytic activity of the entire resin beads over the whole sucrose concentration range. This is shown in Figure 4. The difference increases strongly with the concentration of sucrose. The dependence on the sugar concentration can be explained by a superposition of the acid site strength and a strong decrease of the diffusion coefficient leading to a maximum rate constant around 500 g L$^{-1}$ sucrose. Even in bulk solution the diffusion coefficient of sucrose decreases more than exponentially with the mass fraction of sucrose. High sucrose concentration principally may also cause a film diffusion resistance. It was found to occur at higher temperatures and concentrations during the operation of a fixed bed reactor. However, the reaction rate dependence on the stirring speed was not checked in the current experiments.

### 2.4. Activation energy

Figure 5 shows the plot of the logarithms of the rate constants against the reciprocal absolute temperature. The activation energy of sucrose hydrolysis in the milled C124SH resin is 100 kJ mol$^{-1}$ K$^{-1}$. As expected, that value is nearly equal to the average value reported in the literature for homogeneous acid catalysis which is 107 kJ mol$^{-1}$ K$^{-1}$. Also not surprisingly, the activation energy of sucrose hydrolysis in the entire resin beads is somewhat lower. The value of 80 kJ mol$^{-1}$ K$^{-1}$ indicates that the reaction is partly governed by diffusion. Full diffusion control would require the half value (54 kJ mol$^{-1}$ K$^{-1}$).

### 2.5. Subsequent reaction to HMF

In food technology, 5-hydroxymethyl furfural is an unwanted side product. It is formed by acid catalyzed dehydration of C6-sugars. Ketohexoses are commonly considered to be more reactive than aldohexoses because of easier enolization. Hence, fructose is by a factor of about 100 more reactive than glucose. Brensted acid catalyzed isomerization of glucose to fructose via the acyclic 1,2-endiol provides an alternative slow and indirect pathway to HMF. The fructose based conversion to HMF is proven not to proceed through the acyclic tautomeric

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**Figure 3.** Influence of the mean particle size in water on the apparent sucrose hydrolysis rate constant of resins crosslinked with 4% and 8% dvb using 40% w/w sucrose at 60°C. Curve fit according to Equations (16) and (17).
fructose form in D$_2$O. Instead it starts from the $\alpha$, $\beta$-furanose tautomeric forms which are most favorable to reach the 5-ring HMF after 3 times remove of water. As shown in Scheme 1, due to traditional carbohydrate chemistry and quantum-mechanical calculations, the first acid attack is on the anomic C2 of the $\alpha$,$\beta$ fructofuranose followed by the first reversible dehydration towards the intermediate product (X).

The tautomerization is catalyzed by acids\cite{74} and therefore assumed to be rapid enough to replenish the furanose forms. When all upstream equilibria are reached rapidly enough, a quasi-stationary state is achieved, and the resulting overall kinetics is a first order reaction. According to early investigations of homogeneous acid catalysis\cite{75} that reaction order is commonly assumed in the literature. An order range between 0.8 and 1.35 was derived from the analysis in acid fructose decomposition system to HMF and subsequent products (levulinic and formic acid).\cite{76} Figure A3 in the SI shows a constant initial rate constant without deviations by subsequent reactions for 40 % fructose solution at 60 °C. The HMF formation does not depend on whether the resin is milled or not. Diffusional limitations are absent. A similar behavior is observed in long lasting sucrose hydrolysis at sucrose conversion approximating 100 % (Figure A4 in the SI).

To bridge the gap between pure fructose solutions and sucrose hydrolysis, mixtures of sucrose with fructose, glucose, or sorbitol as a completely inert C6-polyol were subjected to acid resin catalysis. Regarding a 40% sucrose solution hydrolyzed to a residual sucrose content of 7 %, the mass fraction of glucose plus fructose is calculated to be 35 %. Figure 6 shows the evolution of HMF of respective solutions where 35 % non-sucrose matter is completely fructose, glucose or sorbitol. A nearly linearly increasing HMF concentration is found for the mixtures with fructose while mixtures with glucose and sorbitol produce only few HMF. Glucose as source of HMF in sucrose hydrolysis can therefore be neglected. In mixtures with glucose or sorbitol the sparse occurrence of HMF can be explained by the formation of fructose from the hydrolysis of the 7 % sucrose fraction.

To describe the kinetics of HMF formation in sucrose containing reaction mixtures we start with the course of fructose concentration $[F]$ relative to its final value $[F_{\infty}]$ given by:

$$[F] = k_0 \cdot V_{\text{bead}} \cdot [S]$$

where $k_0$ is the hydrolysis rate constant related to the bead volume for milled and entire beads of C124SH (4 % dvb) at 60 °C depending on total sugar concentration.

**Scheme 1.** Reaction sequence due to the literature.
the sucrose hydrolysis rate constant $k_s$ according to Equation (18)

$$[F] = [F]_0 \{1 - \exp(-k_s t)\} \tag{18}$$

Provided the conversion of fructose to HMF is much slower than its formation by sucrose hydrolysis ($k_{\text{HMF}} \ll k_s$), the formation of HMF is [Eq. (19)]

$$\frac{d[HMF]}{dt} = k_{\text{HMF}} \cdot [F] = k_{\text{HMF}} \cdot [F]_0 \{1 - \exp(-k_s t)\} \tag{19}$$

After separation of the variables, integration yields [Eq. (20)]

$$[HMF] = \left(\frac{k_{\text{HMF}}}{k_s}\right) [F]_0 \{k_s t + \exp(-k_s t) - 1\} \tag{20}$$

The rate constants $k_{\text{HMF}}$ are here and in the following related to the sum of all fructose tautomers and not to $\beta$-fructofuranose alone.

Figure 7 shows the application of that rate law on the experimental results. A significant deviation occurs, visible in the logarithmic scale. The deviation is restricted to the low sucrose conversion range where the concentration of fructose increases starting from zero. To overcome that deviation, the existence of a further intermediate compound is assumed here. It is known from a recent publication that associations of fructose may auto-catalyze the splitting of a difructose dianhydride. Therefore, a corresponding existence of fructose-fructose associate or simply a fructose dimer is assumed here as an intermediate product. Consequently, the reaction sequence shown above, which is mostly used in the literature, is changed to the Scheme 2.

The fructose tautomer mixture $F$ is in rapid equilibrium with the $\beta$-fructofuranose which reacts to the fructofuranosyl cation $X^-$ by the slowest rate determining constant $k_s$. This cation is assumed to rapidly react with fructose in excess ($[X^-] \ll [F]$) to a fructosyl dimer $FF$ being a fructose disaccharide, for example inulobiose or another isomer. The dimer is rapidly split into
Figure 6. HMF (per mass of reaction liquid) formed as a function of catalyst mass and time during hydrolysis of sucrose in mixtures with fructose, glucose or sorbitol at 60°C on the S2328 resin.

Figure 7. Test of different HMF kinetic models (see text) for the hydrolysis of 40% w/w sucrose solution on C124SH resin (700 μm) at 80°C.
HMF, fructose, and two H$_2$O. Under the prerequisite that [FF] is proportional to [F] the overall reaction order is 1/2. The formation of HMF is therefore no more defined by Equations (19) and (20). With the overall rate constant being $k_{\text{HMF}} = k_\text{s}$, the HMF concentration increases according to Equation (21).

$$d[F]/dt = -k_{\text{HMF}}[F_{\infty}] \sqrt{1 - \exp(-k_\text{s}t)}$$

As outlined in the SI, the integration yields:

$$\frac{k_{\text{HMF}}}{k_\text{s}}[F_{\infty}] \left\{ \ln \left( \frac{1 + \sqrt{1 - \exp(-k_\text{s}t)}}{1 - \sqrt{1 - \exp(-k_\text{s}t)}} \right) - \sqrt{1 - \exp(-k_\text{s}t)} \right\}$$

Figure 7 shows that the half order reaction of HMF (model 2) yields an acceptable fit to the experimental results. For comparison, another kinetics (model 3) is added. It is assumed there that the fructose dimer is produced in a bimolecular reaction of X and fructose while HMF results in a parallel reaction starting from X. The kinetics is derived in the SI. As expected, the strongest deviation occurs for a second order kinetics of fructose to HMF according to $F \rightarrow FF \rightarrow$ HMF (model 4). The prevalence of the reaction order of 1/2 was found in the analysis of a lot of other experimental examples, also for other reaction conditions in sucrose concentration and temperature (cf. Figure A5 and A6 of the SI). The course of reaction is shown there in mass fractions instead of concentration. This makes no difference, also in case of high concentrated sugar solutions, because the density change during the conversion of sucrose to invert sugar is negligible (< 1 %) (see start of chapter 2.2). The reaction order of 1/2 is used for all further kinetic evaluations throughout this paper.

With respect to the differing order reaction, the rate constants of HMF formation can only conditionally be compared with those for the main reaction. Nevertheless, the temperature dependence of both constants is shown in combination in Figure 5. While the glucose/fructose formation, because of diffusion control, depends on the resin size, this is not the case for HMF. It is formed with an activation energy of 140 kJ mol$^{-1}$ which is inside the range of 120–170 kJ mol$^{-1}$ reported in the literature.[79] That high value is also a result of the fraction of $\alpha_2\beta$-fructofuranose which increases with the temperature.[79]

During the course of sucrose hydrolysis the mass of carbohydrates is nearly constant. What varies, is the carbohydrate composition. The change of fructose fraction was previously shown to cause the 1/2 order reaction. Another topic is the fraction of water. According to Figure 8 the reaction rate constant $k_{\text{HMF}}$ increases exponentially with the total sugar concentration. Compared to the approximate linear increase of the main reaction (Figure 4), the formation of HMF is much more sensitive to water reduction. That effect is well known, and was first observed by Kuster.[79] when replacing water by polyethylene glycol in the homogeneous acid dehydration of fructose to HMF. One may assume that this effect reflects an increase of the $\alpha_2\beta$ fructofuranose tautomer fraction. But literature data points out to an uninfluenced tautomer fraction up to 80 % aqueous fructose solution.[80] Only the change to other solvents than water can have an effect in that direction.[79]

The strong enhancement of HMF formation by water reduction compared to its effect on sucrose hydrolysis is simply that HMF is less hydrophilic than sugar. Hence its occurrence is stabilized, in addition to the effect of acidity enhancement. A significant effect of the catalyst size and diffusion is absent, also at high sugar concentration.

Up to now it was tacitly presumed that the rate constant of HMF formation is independent on the nature of sugars inside the total carbohydrate fraction. Some experiments, those of Figure 6 and others, were performed in that direction by sucrose hydrolysis with different fractions of admixed fructose. Data shown in the SI (Figure A7) point out that pure fructose has an about 30 % greater rate constant than fructose occurring together with other sugars (sucrose, glucose). That positive cooperative effect is not actually understood. It needs to be investigated in homogeneous acid catalysis, too. Otherwise, resin specific effects may be the reason, for example different distribution equilibria inside the system of resin and external liquid, as already remarked in chapter 2.2. The main reaction is nearly uninfluenced by that effect (Figure A8).

### 2.6. Color formation

Besides HMF the formation of colored side products is unwanted in the industrial sucrose hydrolysis. Mostly color occurs in food technology as a consequence of the Maillard reaction, describing a system of reactions starting with the interaction of carbohydrates with amino acids. A part of those reactions proceeds without amino acids and is called caramelization.[81] Here we have to consider pure acid-catalyzed caramelization. Key compounds of that complex system are 5-hydroxymethylfurfural, 2-hydroxyacetofuran, and 3,5-Dihydroxy-2-methyl-5,6-dihydroxypyran-4-one.[82] Formation of caramel colors is related to the formation of humins currently of interest as by-product in the isolation of bulk HMF.[82] The color of an acid HMF mixture changes from dark brown to black during storage, until the emergence of humic solids.[82] Caramelization can therefore be regarded as a very early stage of the evolution of high polymeric humins.[82]
In sugar technology, color is measured by absorbance at 420 nm as standard.\textsuperscript{38} The result of such measurements during sugar hydrolysis at different temperatures is shown in Figure 9. In order to focus the sucrose hydrolysis on the HMF formation, sucrose was mixed with fructose, as already discussed for Figure 6. Measuring the absorbance and the HMF concentration results in Figure 9 A. Surprisingly for 3 different temperatures a single curve is obtained which suggests that the color is only a function of HMF. In other words: the activation energy of color formation is the same as that of HMF.

However, the comparison with data from the literature\textsuperscript{84} at first prompts an accidental independence on the temperature.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Rate constant of HMF formation related to the bead volume for milled and entire beads of C124SH (4\% dvb) at 60 °C depending on sucrose concentration.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Color development (absorbance at 420 nm) during sucrose hydrolysis as a function of HMF development at 3 different temperatures. A) 7\% sucrose + 35\% fructose at S2328 sulfonic acid resin. B) 18.5\% fructose, homogeneous catalysis at pH = 3. Literature data.\textsuperscript{84}}
\end{figure}
As shown in Figure 9 B, the measurements obtained with pure solution of only 19% w/w fructose at pH = 3 shows positively bent curves, too. But the ratio of color per HMF decreases with increasing temperature, which means that the color formation has a significantly lower activation energy compared with that of HMF. The authors claimed 66 kJ mol\(^{-1}\) against 160 kJ mol\(^{-1}\) of their HMF formation.\[85\]

A better explanation regarding the difference between Figure 8 A and B refers to the high polymeric nature of the colored substances. The color of liquid sugar can be removed in industrial scale by polysulfone ultrafiltration membranes having a molecular mass cut-off in the range of 1 to 20 kDa.\[85,86\] During the resin catalysis only the low molecular intermediate products are formed inside the beads. Higher molecular colored substances can then solely be formed outside where the acid concentration is comparably negligible. As a result, the final steps of color formation are slowed down and the total activation energy is limited by that of HMF being the fastest first step.

One may argue that the reported absorption at 420 nm is reduced by adsorption of these high molecular substances on the resin surface. However, this can be excluded because the colored material contains some carboxylic acid groups and apart from that is mainly hydrophobic. Hence, decolorization is achieved in the industrial scale by adsorption on strongly basic macroporous ion-exchange resins in the chloride form and desorption by strong alkaline solutions.\[85\] Adsorption on sulfonic acid resins is not reported and only non-functionalized styrene-dvb resins can adsorb color by hydrophobic interaction.\[87\]

### 2.7. Reversion products

Figure 10 shows an example of the development of all products discussed so far at high initial concentration of sucrose (75% w/w). Three different runs (A, B, C) document sufficient reproducibility. Remarkable is that the saturation value of fructose is significantly lower than that of glucose. That difference gradually diminishes with lowering sucrose concentration (cf. Figure A9 SI). The existence of that effect is well known in industrial sucrose hydrolysis plants. The loss of fructose must be due to the formation of reversion products. These products occur by back reaction of the monosaccharides to disaccharides others than sucrose differing in saccharide composition and glycosidic linkage.\[29\] Their occurrence increases with rising carbohydrate concentration and can even produce oligosaccharides. Since aldoses, such as glucose, are less reactive than ketoses, such as fructose, the reversion products are expected to contain fructose in majority. While the (1→2) β linkage of inulobiose and the (1→6) β bond of levanbiose occur in living systems, more isomers of fructose disaccharides are accessible by pure acid catalysis. Also possible is the reaction of fructose with glucose leading to sucrose isomers. At last, fructose can be added to sucrose forming the group of kestoses. Only fructose containing disaccharides can further condense to difructose dianhydrides.\[32,33\]

![Figure 10](image)

**Figure 10.** Reaction of a 75% w/w solution of sucrose on C124SH resin (68 μm) at 60°C. Three different experiments (A, B, C). Regression of fructose and glucose according to Equation (18) and of HMF according to Equation (22)
Assuming that the majority of reversion products consists of disaccharides of fructose, at first, results concerning the action of sulfonic acid resins on high concentrated fructose solutions are presented. These compounds occur in the hydrophilic interaction HPLC directly after the peak of fructose, not resolved but as a superposed group (Figure A10). Figure 11 shows the development of these products. The hyperbolic course suggests that the reaction attains an equilibrium value. Compared to the concentration of fructose, which decreases only slightly from the initial value of 700 g kg\(^{-1}\), their equilibrium concentration is 56 g kg\(^{-1}\). The total mass of fructose and non-fructose compounds is shown to be constant within ±1.2 % in this experiment. Since no glucose is present, one can assume that these products are formed by dimerization of fructose. That must be a second order reaction while the decomposition of the dimers to fructose is of first order. As derived in the SI, the kinetics of that reaction is given by Equation (23)

\[
x(t) = \frac{x_\infty (1 + \alpha) [1 - \exp(k_1 \alpha x_\infty t)]}{1 + \alpha - \exp(k_1 \alpha x_\infty t)}
\]  

(23)

where \(k_1\) is the dimer formation rate constant, \(x\) is the concentration of all dimers, \(x_\infty\) is the equilibrium concentration and \(\alpha\) a parameter linked to the initial fructose concentration \(c_{fo}\) by Equation (24)

\[
\alpha + 1 = \left( \frac{c_{fo}}{x_\infty} \right)^2
\]  

(24)

It is known that the back-reaction \((k_2)\) is catalyzed by fructose,\(^{[73]}\) but fructose is present in the reaction mixture and it is supposed to be sufficiently enough for a constant value of \(k_2\). The green curve in Figure 11 is calculated by nonlinear regression of these equations to the experimental points. While the the reversion products of pure fructose are following the first appearing fructose peak in hydrophilic interaction chromatography, these peaks are superposed by the large glucose and sucrose peaks in sucrose hydrolysis. In order to solve that separation problem, and old method relying on the fermentation of the different sugars containing samples by baker’s yeast to ethanol\(^{[89]}\) has been recommended in a much later publication\(^{[31]}\) as completion of modern separation techniques. The yeast can completely metabolize common saccharides such as sucrose, glucose, and fructose\(^{[85]}\), while more seldom saccharide derivatives are resistant. Figure A10 of the SI shows how that treatment affects the carbohydrate analysis by the hydrophilic interaction chromatography: a pure sucrose sample is completely metabolized to ethanol occurring near the injection peak followed by some other smaller peaks belonging to yeast, while a certain DFA isomer (DFA III) remains uninfluenced. Due to the literature the resistance of DFA III can be extended to a lot of other isomers\(^{[33,90]}\), but inulobiose\(^{[91]}\) as a fructose containing disaccharide, inulotriose\(^{[92]}\), and also glucose containing (1→2) β linked fructooligosaccharides (1-kestose, nystose)\(^{[93]}\) are metabolized. Hence, the application of that method to side product analysis in sucrose hydrolysis is expected to be incomplete. Indeed, when applied to the reaction of a high concentrated fructose solution on a sulfonic acid resin, the product analysis by hydrophilic interaction HPLC at milled C124SH resin (0.99 g per kg solution) to reversion products at 60 °C. green: original HPLC analysis, blue: after yeast treatment, red: HMF. Lines following non-regressions according to Equations (23,24).
shows that not all reversion products occurring after the fructose peak are retained after treatment with yeast (Figure A11, S1). According to Figure 11 the application of the kinetic model (Equation 23, 24) to the yeast treated samples yields an equilibrium concentration of fructose reversion products reduced to the half (26 g kg\(^{-1}\)). Since no further tests with other fructose dimers than inulobiose are neither available in the literature nor performed in the present study, it can only be preliminary assumed that enzymatically accessible fructose disaccharides are metabolized and all other not. The values obtained after metabolization of fructose by yeast correspond therefore to DFA spirocompounds plus “some” disaccharides totally composed of fructose. The yeast treatment for reversion product analysis is expected to be incomplete in sucrose hydrolysis, too. As shown in Figure A12, the typical HPLC diagram obtained after yeast treatment is different to that of fructose reversion products because the presence of glucose enables the formation of mixed glucose-fructose disaccharides (sucrose isomers) in addition.\(^{29}\) Corresponding analyses of the hydrolysis of other high concentrated sucrose solutions are presented in Table 2. The content of yeast resistant reversion products is found to be in the same order of magnitude of those occurring in pure fructose solutions (Figure 11). Table 2 contains analyses of industrially produced invert sugar, as well. The applied processing include treatment with active carbon for decolorization which also reduce HMF, but the reversion products remain uninfluenced being in the same order of magnitude as those of the present work. When the sugar concentration is lower than 70% w/w, simple yeast treatment followed by common HPLC fails because the concentration of reversion products is too low. Therefore, another analytical method based on carbohydrate silylation and gas chromatography was applied. That method is able to resolve the single isomers, and due to the literature, the assignment of the single peaks to the chemical structure by carbohydrate silylation and correlates about linearly with the literature, it can only be preliminary assumed that enzymatically accessible fructose disaccharides are metabolized and all other not. The values obtained after metabolization of fructose by yeast correspond therefore to DFA spirocompounds plus “some” disaccharides totally composed of fructose. In accordance with the literature,\(^{32}\) the most occurring isomer is number 9 (\(\alpha\-D-frucf-1,2\'-2,1\'-\beta\-D-fruc\)). Some fractions are decreasing, others increasing with time, indicating that the equilibrium between the isomers is not yet reached (Figure A15, A16). Besides the DFAs, the applied GC method detects also some fructose disaccharides. They are formed in an extent of 40 to 80% of the detected DFAs. However, their assignment to the retention time of the GC analysis is still missing and not described in the literature. The occurrence of silylated sucrose including some incomplete silylated sucrose affects the method, but yeast treatment followed by GC-analysis\(^{33}\) was tried to be avoided here.

Results are shown in Figure 12. All 40% w/w carbohydrate solutions produce DFAs. The sum of the detected species is around some mg kg\(^{-1}\) and correlates about linearly with the formation of HMF. The lowest slope is obtained for 80°C (grey line) while at 60°C the ramp is greater (blue line). Therefore, the activation energy of the fructose dimerization has to be lower than that of fructose conversion to HMF. These experiments (blue line) belong to invert sugar of 20% fructose and 20% glucose and to the reaction mixture during hydrolysis of 40% sucrose solution. When the experiment is done with 40% pure fructose, the slope is much more enlarged (orange line) and the curve is bent at higher HMF concentration in order to reach the equilibrium state earlier.

### 2.8. Leaching

In addition to the interpretation of the reaction kinetics presented so far, important remarks to the experimental design have to be reported here. Leaching of ion-exchange resins can have a severe impact on their catalytic action, especially in batch experiments. An example, reported in the literature, is related to the use of a sulfonic acid resin in the conversion of fructose to DFA.\(^{34}\) The authors state in the experimental part that after simplified conditioning by washing with water-HCl-water the catalytic activity observed in the first use of that catalyst at 90°C was only recovered at about half by repeated washing. The authors assumed an unknown deactivation process. But more probable is a partial shift of the locus of reaction from the resin interior to the outer phase by the release of more efficient free acid, an effect occurring less when the resin is freshly recovered after use.

| Sample | Inversion [%] | \(c_1\) [g kg\(^{-1}\)] | \(c_2\) [g kg\(^{-1}\)] | Fructose [g kg\(^{-1}\)] | Glucose [g kg\(^{-1}\)] | Sucrose [g kg\(^{-1}\)] | HMF [g kg\(^{-1}\)] | Rev. prod. [g kg\(^{-1}\)] |
|--------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Bead   | 91             | 750             | 310             | 372             | 68.4            | 1.17            | 25.80 ± 0.75    |
|        | 85             | 700             | 288             | 322             | 107             | 0.382           | 11.72 ± 1.32    |
|        | 99             | 750             | 352             | 387             | 4.7             | 0.338           | 11.32 ± 0.78    |
|        | 61             | 750             | 237             | 249             | 290             | 0.042           | 4.77 ± 1.19     |
|        | 72             | 723             | 260             | 275             | 201             | 0.044           | 7.66 ± 1.35     |
|        | 99             | 711             | 339             | 361             | 5.2             | 0.026           | 33.75 ± 1.78    |

[a] Determined after digestion with yeast, [b] sugar concentration \(c_1\) as delivered, [c] initial sucrose concentration \(c_2\). Values for industrial samples are calculated based on the absence of dilution or evaporation steps.

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In the present work all resins were additionally washed with methanol which causes a better solvent-resin interaction with the non-polar polystyrene backbone. By that way not only red colored impurities but also acid substances were removed. Probably these impurities consist of only physically bound (sulfonated) polymer fragments which should result from the industrial polymerization process. However, also when these substances are removed during a 4-day lasting washing procedure at room temperature, the afterwards stored wet samples were shown to release further acid impurities detectable after storage for some weeks. Obviously that process is controlled by diffusion barriers inside the resin, but oxidation is discussed, too.[95] Microbial desulfonation[96] is another possibility to be taken into account. The release of acid organic compounds from resins during cellulose hydrolysis[97] and in demineralization plants over years has already been reported.[98,99] Such an instability, apart from thermally induced release of really covalently bound acid groups by reverse sulfonation,[100] may also play a role in morphological changes of resins during several year operation as catalysts.[101] The leaching observed during the present study was not systematically investigated. The pH of the hydrolysis reaction mixture was controlled to be greater than 5 at the end of the reaction. The effect of that pH reduction may stem from residual ash content of the sugar which releases protons by partial ion-exchange with the sulfonic acid groups. But removing ash from the initial sugar solution, either by re-crystallization or ion-exchange at low temperature, has shown an effect on resin catalysis only in case of high concentrated sugar. Limited times of wet resin storage was found to be most effective to minimize the pH reduction of the reaction mixture. The impact of leaching is especially great when the actual resin turn-over number is low, for example in case of high concentrated sucrose solution or carbohydrate polymers such as inulin. Further investigations of aqueous media resin catalysis require the improvement of the conditioning procedure by continuous hot extraction. The influence of possible leaching has to be considered during the assessment and discussion of already published results.

3. Conclusion

The hydrolysis of sucrose catalyzed by sulfonic acid ion-exchange resins has been intensively investigated in the past. However, the formation of by-products such as DFAs, HMF, and color has not been addressed in detail, and previous investigations are limited to sugar concentrations lower than 50% although sucrose is soluble in water up to 79% at 80°C. Increasing sugar concentration alters the solvent properties drastically. Not only viscosity is increased and sucrose mobility decreased even in bulk solution, but also the reaction rate constants, based on the proton concentration, are changed. HMF is an important target product in green carbohydrate-based chemistry. The knowledge of HMF formation during sucrose hydrolysis can therefore be understood as a bridge to those processes where the subsequent decomposition of HMF to levulinic acid, formic acid and humins begin to dominate. In the present work, a thorough kinetic analysis of sugar hydrolysis over sulfonic acid resins is presented, based on the interdependence of HMF formation and sucrose hydrolysis where the subsequent complicating reactions, mentioned above, can be neglected. HMF is clearly shown to be formed due to a 1/2 order reaction in fructose. This order can be explained by the existence of a fructose disaccharide and its decomposition to fructose and HMF. The finding contradicts the proposal of Tsai et al.[102] that DFAs may serve as key intermediate for the conversion of fructose to HMF. The formation of DFA parallels that of HMF and is found to be a classical second order reaction. In addition to the effect of the reaction order, reduced water concentration has an impact, too. Another fraction of side products comprises fructose disaccharides (FD) with not yet
analyzed different glycosidic linkage. Among the side reactions the fraction of DFAs and other reversion products is by far the most important. It can amount to some per cent in technical invert sugar solutions and is expected to influence the direct conversion of fructose to HMF, too.

The formation of color is the fourth reaction caused by the reactivity of fructose. Macromolecular colored substances are interpreted as early precursor of humic acid. Compared to homogeneous acid catalysis their polymerization inside the resin is limited by steric reason.

All these fructose-based reactions are found to be unlimited by diffusion of fructose inside the sulfonic acid resin beads. The findings reported here, can therefore most likely be transferred to homogeneous acid catalysis. In contrast, the hydrolysis of sucrose is much more rapid. While the rate constant per resin volume increases linearly with the total sugar concentration in the case of size-reduced resins, the macro-kinetics of the entire resin beads is considerably slowed down by diffusional limitation. At around 40% w/w sugar the hydrolysis rate constant is maximal.

Further work is needed to specify the interplay of fructose, HMF, fructose disaccharides, DFAs, and water. Since the DFAs consist of 14 diastereomers and several disaccharide isomers HMF, fructose disaccharides, DFAs, and water. Since the DFAs is maximal.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acid catalysis · fructose · inulobiase · difructose dianhydride · 5-hydroxymethylfurfural

[1] S. Peters, T. Rose, M. Moser, Top. Curr. Chem. 2010, 294, 1–23.
[2] That value was extrapolated from data concerning the European Suedzucker company. Annual report of Suedzucker AG 2012/13.
[3] H. W. Jung, Saccharose, in Handbuch der Süßungsmittel (Eds.: K. Rosenplenter, U. Nöhle), Behr’s Verlag, Hamburg, 2007, pp. 103–104.
[4] H. Schieweck, M. Clarke, G. Pollach, Sugar in Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2007.
[5] T. L. Mega, R. L. van Etten, J. Am. Chem. Soc. 1988, 110, 6372–6376.
[6] S. Yamabe, W. Guan, S. Sakaki, J. Org. Chem. 2013, 78, 2527–2533.
[7] A. D. Pethbridge, J. Chem. Soc. A 1969, 1345–1350.
[8] L. P. Hammett, M. A. Paul, J. Am. Chem. Soc. 1934, 56, 830–832.
[9] C. Kalidas, S. R. Paitt, J. Chem. Soc. 1961, 3998–4006.
[10] C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, C. A. Vernon, J. Chem. Soc. 1957, 2327–2334.
[11] K. Vukov, Int. Sugar J. 1965, 67, 172–175.
[12] S. Buchanan, D. Kubler, C. Meigs, M. Owens, A. Tallman, Int. J. Chem. Kinet. 1983, 15, 1229–1234.
[13] J. Szejtli, Acid hydrolysis of glycosidic bonds [in German], VEB Verlag, Leipzig, 1976.
[14] J. Szejtli, R. D. Henriques, M. Castineira, Acta Chim. Sci. Hung. 1970, 66 213–227.
[15] E. Marianii, Ann. Chem. Appl. 1949, 39, 283–290.
[16] G. Bodamer, R. Kunin, Ind. Eng. Chem. 1951, 43, 1982–1085.
[17] N. Lifshutz, J. S. Dranoff, Ind. Eng. Chem. Fundam. 1966, 7 266–269.
[18] S. H. Khan, K. Rahman, Chem. Eng. J. 1996, 61, 7–12.
[19] E. R. Gilliland H J Bixler, J. E. O’Connell, Ind. Eng. Chem. Fundam. 1971, 10 185–191.
[20] J. Nowak, K. Gedicke, D. Antos, W. Piatowski, A. Seidel-Morgenstern, J. Chromatogr. A 2007, 1164, 224–234.
[21] G. Siegers, F. Martinola, Int. Sugar J. 1985, 87, 23–26.
[22] K. Abraham, R. Gurlt, K. Berg, G. Heinemeyer, A. Lampen, K. E. Appel, Mol. Nutr. Food Res. 2011, 55, 667–678.
[23] S. L. Chen, D. J. Yang, H. Y. Chen, S. C. Liu, Food Chem. 2009, 114, 582–588.
[24] W. C. Yoo, N. Rajabbeigi, E. E. Mallon, M. Tsapatsis, Microporous Mesoporous Mater. 2014, 184, 72–82.
[25] C. Detoni, C. H. Gierlich, M. Rose, R. Palkovits, ACS Sustainable Chem. Eng. 2014, 2, 2407–2415.
[26] G. B. M. Carvalho, S. I. Musatto, E. J. Candido, J. B. Almeida e Silva, J. Chem. Technol. Biotechnol. 2006, 81, 152–157.
[27] H. Hattori, K. Tajima, H. T. Chang, T. Murayama, E. Furuya, Adsorption 2005, 11, 917–920.
[28] P. Thavarajah, N. H. Low, J. Agric. Food Chem. 2006, 54, 2754–2760.
[29] K. W. Swallow, N. H. Low, J. Agric. Food Chem. 1993, 41, 1587–1592.
[30] P. F. Cancalon, J. AOAC Int. 1993, 76, 584–590.
[31] A. I. Ruiz-Matute, O. Hernández-Hernández, S. Rodríguez, M. L. Sanz, I. Fernández, K. de Pliva-Vigier, J. Agric. Food Chem. 2011, 61, 175–177.
[32] M. Audemar, L. Atencio-Genes, C. Ortiz Mellet, F. Jérôme, J. M. Garcia-Fernández, K. de Pliva-Vigier, J. Agric. Food Chem. 2007, 55, 7264–7269.
[33] M. R. Antonio-Garcia, A. Y. Sanz, J. Agric. Food Chem. 2007, 55, 7264–7269.
[34] B. Herbreteau, M. Lafosse, L. Morin-Allory, M. Dreux, Carbohydr. Res. 2007, 342, 325–330.
[35] S. Albalá-Hurtado, M. T. Veciana-Nogués, M. Izquierdo-Pulido, M. C. Vidal-Carou, J. Agric. Food Chem. 1997, 45, 2128–2133.
[36] W. Mauch, Quality criteria of white Sugar and its commercial grades, Analytical methods, in Sugar Technology (Eds.: P. W. van den Poel, H. Schiweck, T. Schwartz) Albert Barten, Berlin, 1998, p. 94.
[37] S. H. Yoon, R. Mukerjea, J. F. Robyt, Carbohydr. Res. 2003, 338, 1127–1132.
[38] A. J. Ruiz-Matute, O. Hernández-Hernández, S. Rodríguez, M. L. Sanz, I. Martinez-Castro, J. Chromatogr. A 2007, 1164, 727–732.
[39] G. H. Fricke, D. Rosenthal, Anal. Chem. 1971, 43, 648–656.
[40] K. W. Pepper, D. Reichenberg, D. K. Hale, J. Chem. Soc. 1952, 3129–3136.
[41] S. Liu, Y. Li, S. Shen, Q. Xiao, L. Chen, B. Liao, B. Ou, Y. Ding, J. Appl. Polym. Sci. 2011, 121, 654–659.
[42] B. N. Kolmar, P. Wieczorek, Angew. Makromol. Chem. 1991, 185–191.
[43] R. Bringué, E. Ramírez, M. Ibára, J. Tejero, F. Cunill, J. Catal. 2013, 304, 7–13.
[44] Z. Bubnik, P. Kadlec, D. Urban, M. Bruhns (Eds.), Sugar Technologist’s Manual, Barten, Berlin, 1996, pp. 134–136, 171, 175.
[45] M. Rampp, C. Buttersack, H. D. Lüdemann, Ind. Eng. Chem. Res. 2000, 39, 4400–4407.
[46] M. Rampp, C. Buttersack, H. D. Lüdemann, Carbohydr. Res. 2000, 328, 561–571.
[47] T. Moran, W. C. M. Lewis, J. Chem. Soc. 1922, 121, 1673–1684.
