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► To cite this version:

Imelda Elizabeth Ortiz-Cerda, Phahath Thammavong, Vincent Caqueret, Catherine Porte, Isabelle Mabile, et al.. Synthesis of Prebiotic Caramels Catalyzed by Ion-Exchange Resin Particles: Kinetic Model for the Formation of Di- d -fructose Dianhydrides. *Journal of Agricultural and Food Chemistry*, 2018, 66 (7), pp.1693-1700. 10.1021/acs.jafc.7b04868 . hal-01757786

HAL Id: hal-01757786

<https://hal.science/hal-01757786v1>

Submitted on 26 Sep 2024

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Article

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J. Agric. Food Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.jafc.7b04868 • Publication Date (Web): 27 Jan 2018

Downloaded from <http://pubs.acs.org> on January 28, 2018

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1 **Synthesis of prebiotic caramels catalyzed by ion exchange resin particles: kinetic model**
2 **for the formation of di-D-fructose dianhydrides**

3

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17

18 **Keywords**

19 Prebiotic caramel, difructose dianhydride, kinetic law, fructose, heterogeneous catalysis.

20

21

22 **ABSTRACT**

23 Caramel enriched in di-D-fructose dianhydrides (DFAs, a family of prebiotic cyclic
24 fructodisaccharides) is a functional food with beneficial properties for health. The aim of this
25 work was to study the conversion of fructose into DFAs catalyzed by acid ion-exchange resin,
26 in order to establish a simplified mechanism of the caramelization reaction and a kinetic
27 model for DFA formation. Batch reactor experiments were carried out in a 250 mL spherical
28 glass flask and afforded up to 50% DFA yields. The mechanism proposed entails order 2
29 reactions that describe fructose conversion on DFAs or formation of by-products such as
30 HMF or melanoidins. A third order 1 reaction defines DFA transformation into fructosyl-
31 DFAs or fructo-oligosaccharides. The influence of fructose concentration, resin loading and
32 temperature was studied to calculate the kinetic parameters necessary to scale up the process.

33

34

35 INTRODUCTION

36 The current increase in the frequency of some chronic diseases such as cardiovascular
37 diseases, obesity, diabetes and certain types of cancer, in particular colon cancer, is linked to
38 environmental issues among which nutrition plays a prominent role. Indeed, nutrition is
39 becoming a major public health issue. The food industry therefore offers innovative solutions
40 to improve the quality of products by adding beneficial health substances such as
41 antioxidants, vitamins and prebiotics. In this context, di-D-fructose dianhydrides (DFAs), a
42 complex family of cyclic fructodisaccharides with prebiotic activity present in caramel^{1,2}
43 provide an innovative option. A prebiotic is defined as "a non-digestible food ingredient that
44 beneficially affects the host by selectively stimulating the growth and/or activity of one or a
45 limited number of bacteria in the colon, thus improving the host health". New processes have
46 been proposed to enhance the proportion of DFAs in caramel, among which caramelization of
47 fructose at relatively low temperature (80-100 °C) catalyzed by ion exchange resin particles is
48 particularly attractive in view of industrial development.³⁻⁵ Fructose is one of the most
49 abundant monosaccharides and is known to be the sweetest natural sugar.⁶

50 Formation of DFAs under caramelization conditions competes with unspecific dehydration
51 reactions of the starting sugar, which is essentially related to the formation of 5-
52 (hydroxymethyl)furfural.⁷⁻¹⁰ The kinetics of DFA formation have been investigated under
53 various conditions. Thus, Chu and Berglund¹¹ determined the rate of DFA formation during
54 fructose crystallization and Idri et al.¹² studied the synthesis of prebiotic DFA-enriched
55 caramels assisted by microwave. Caramelization is a complex phenomenon in which many
56 reactions occur, involving several reactional intermediaries (Figure 1). As a result, obtaining
57 an average rate of DFA production is not straightforward. Two approaches have been used to
58 caramelize a sugar: heating at temperatures about the melting point, often in the presence of
59 an homogeneous acid promotor^{11,13} or using a heterogeneous solid catalyst as caramelization

60 promotor, which allows lowering the temperature¹⁴. The second approach has proven
61 preferable in order to obtain DFA-enriched caramels for which prebiotic properties have been
62 evidenced in several animal models¹⁵⁻¹⁹. Although the heterogeneous conditions further
63 complicate a kinetics analysis of DFA formation, several studies indicate that homogeneous
64 models generally provide satisfactory results. For instance, Shan et al.²⁰ studied the hydration
65 of cyclohexene in the presence of an ion exchange resin and zeolites and found that a model
66 representing a homogeneous system best fitted their experimental data. Other authors^{21,22}
67 proposed a pseudo-homogeneous model to describe the esterification and transesterification
68 kinetics catalyzed by an Amberlite® or Lewatit® ion exchange resin. As attested by several
69 studies which compared the reaction kinetics in heterogeneous and homogeneous media^{23,24}
70 the reaction kinetics of certain species resulting from a heterogeneous mixture can be modeled
71 by equations generally applied to reactions used in a homogeneous medium. In line with those
72 antecedents, the objectives of the present study are twofold: to propose a simplified
73 mechanism to describe in a general way the production of DFAs, and to calculate the kinetic
74 parameters of the caramelization reaction catalyzed by resin particles in order to obtain kinetic
75 laws, which can be used in the modelling, design and operational conditions of a reactor.

76

77 **MATERIALS AND METHODS**

78 **Products**

79 Anhydrous D-fructose (99% purity) was purchased from Danisco Sweeteners (Paris, France).
80 The ion-exchange resin Lewatit® S2328, designed for food-products, was purchased from
81 Lanxess (La Wantzenau, France). It is a strongly acidic, macroporous resin exposing sulfonic
82 acid groups that has proven very efficient to promote caramelization processes. The average
83 particle size is between 0.4 and 0.5 mm. Phenyl- β -D-glucopyranoside (Internal standard, I.S.),
84 pyridine, hydroxylamine, hexamethyldisilazane and trimethylchlorosilane were purchased

85 from Sigma–Aldrich. Di- α -D-fructofuranose 1,2':2,3'-dianhydride (DFA 1), α -D-
86 fructofuranose β -D-fructopyranose 1,2':2,1'-dianhydride (DFA 9) and α -D-fructofuranose β -
87 D-fructofuranose 1,2':2,1'-dianhydride (DFA 10) were synthesized and purified at Instituto
88 de Investigaciones Químicas (CSIC – Universidad de Sevilla) following previously reported
89 procedures^{25–27}.

90

91 **Reaction and experimental setup**

92 The Lewatit® S2328 ion-exchange resin (250 g) was stacked in a glass column and
93 subsequently eluted (3 - 4 mL min⁻¹) with deionized water (1 L), 1 M aqueous HCl (1 L) and
94 deionized water (2 L). Drying was first carried out under air current at room temperature and
95 then in an oven at 90 °C for 16 h.

96 The resin exchange capacity was studied in the laboratory²⁸ and showed that i) after use for a
97 two-hour experiment, the resin was almost completely inactivated, ii) its reactivation is only
98 partial with the method used, and an identical conversion of fructose during the second use is
99 not obtained nor a production of similar DAF, which is reduced by one third. Table 1 shows
100 that the fructose conversion is similar for the second use of the resin but is very weak for the
101 third use (even if resin is regenerated after each new use). Moreover, kinetics of DFAs
102 formation is becoming slower and the yield of these compounds decreases. These various
103 tests have shown that the resin loses its exchange efficiency and is exhausted during the
104 reaction. In order to be able to reuse it, it is necessary to regenerate it by methods other than
105 simple washing followed by an activation acid.

106 Batch reactor experiments were carried out in a 250 mL spherical glass flask equipped with a
107 coil condenser to prevent any loss of product and heated by a silicon oil bath controlled by a
108 thermal sensor Pt 100 connected to a hotplate. The mixture was mechanically stirred at 150
109 rpm. The reference conditions were based on the study of Suárez-Pereira et al.¹⁴: fructose

110 mass fraction of 0.9, water mass fraction of 0.1, temperature of 90 °C and resin quantity of
111 0.18 w/w_{mixture}. The effect of fructose mass fraction (0.9, 0.8, 0.7), temperature (70, 80, 90 °C)
112 and resin fraction (0.09, 0.18, 0.27 w/w_{mixture}) were studied. Kinetic monitoring was
113 performed by collecting aliquots at different times (0, 5, 15, 30, 60, 120 min) in 2 mL
114 Eppendorf tubes. The caramelization reaction was stopped by a thermal shock ($T < 50$ °C).
115 The caramel samples were stocked in a 0 °C bath before their derivatization and gas
116 chromatography (GC) analysis.

117

118 **Analysis**

119 GC analyses were carried out using an Agilent 7820A series gas chromatograph equipped
120 with an FID detector (Agilent Technologies). A crosslinked 5% phenyl-dimethylsiloxane
121 column (HP-5; 30 m × 320 μm × 0.25 μm) was used. Operating conditions were: injection
122 port temperature: 310 °C; splitting ratio 25:1; injection volume 1 μL of derivatized samples;
123 column oven temperature programmed from 180 to 310 °C at 5 °C min⁻¹, with a 25 min hold
124 at 310 °C; carrier gas helium (constant flow at 1.2 mL min⁻¹); detector port temperature 310
125 °C. Total acquisition time was 31 min. Caramel samples, as well as the reference samples
126 used for identification, were converted into their corresponding per-O-trimethylsilyl (TMS;
127 non-reducing sugars) or per-O-trimethylsilylated oxime (TMS-oximes; reducing sugars)
128 derivatives following the method described by Sweeley et al.²⁸ Samples were diluted with
129 deionized water (1 mL), the resin (in caramel cases) was separated by centrifugation (6,000
130 rpm, 10 min) and the aqueous solutions were freeze-dried. The dried sugar or caramel was
131 diluted in deionized water to a concentration of 16 mg mL⁻¹. 100 mL of this solution were
132 collected and 100 mL of a solution of phenyl-β-D-glucopyranoside (4 mg mL⁻¹ in acetone-
133 water, 1:9; v/v) were added. This solution was freeze-dried at -60 °C. The residue was then
134 oximated by treatment with 1 mL of a solution of hydroxylamine in pyridine (20 mg mL⁻¹) at

135 60 °C for 50 min. The cooled sample was then trimethylsilylated by reaction with a mixture
136 of hexamethyldisilazane (200 mL) and trimethylchlorosilane (100 mL) at 60 °C for a further
137 40 min period. Formation of a white precipitate was observed during this operation, which
138 was separated by centrifugation (6,000 rpm, 5 min) before injection in the GC apparatus. It is
139 worth noting that following oximation-trimethylsilylation derivatization, reducing compounds
140 (e.g., residual D-fructose and HMF) provide two peaks in the GC chromatograms,
141 corresponding to the syn- and anti-TMS-oximes, while non-reducing derivatives (e.g., DFAs
142 and the I.S.) provide a single peak.¹⁴ Calibration lines were established from pure fructose and
143 DFAs 1, 9 and 10. Injections were repeated three times. Quantification was done by the
144 internal standard method. Response factors (RF) for fructose (RF = 1.26) and four individual
145 DFAs were determined and used for quantification of their relative proportions in caramels.
146 The results compare well with those previously reported by Idri et al.⁴ As the various RF
147 values for different DFA samples were very similar, an average RF value of the different
148 isomers was calculated and used for quantitative estimation of the ensemble of DFAs (RF =
149 0.88), following the method developed by Suárez-Pereira et al.¹⁴

150 Figure 1 presents the chemical structure of DFAs. Numbering follows the order previously
151 used in the literature and is consistent with the elution profile in gas chromatography.¹⁴
152 Number 8 skipped because it denotes a fructose-glucose mixed dianhydride present only in
153 sucrose caramel, which is not the object of the present study.

154 To compare the caramel produced under different conditions, the remaining amount of
155 fructose and DFA yield in the sample was normalized. In Figures 3 to 5, mass fructose
156 proportion and DFA proportion of each aliquot were respectively calculate by %Fructose =
157 $m_{\text{Fructose}}/m_{\text{Fructose}_0}$ and %DFAs = $m_{\text{DFAs}}/(m_{\text{Fructose syrup}})$.

158

159 RESULTS AND DISCUSSION

160 A complete mechanism to describe fructose transformation under caramelization conditions
161 implies about one hundred reactions.²⁹ Considering that under the caramelization conditions
162 used in this study DFA formation is strongly favored over unspecific dehydration, a
163 simplified mechanism is proposed to describe the degradation of fructose, leading to DFA
164 products (path A) and by-products such as HMF and melanoidins (path B). In path C, DFAs
165 are consumed to give fructosyl-DFAs or fructo-oligosaccharides through glycosylation
166 (reversion) reactions. The simplified mechanism of the reaction is shown in Figure 2. This
167 simplified mechanism was used to evaluate the kinetic reaction profile and to calculate the
168 kinetic coefficients of fructose consumption and the production of DFAs.

169

170 **Reaction orders**

171 Christian et al.²⁹ studied independently the kinetics of degradation of each DFA formed from
172 inulin. The DFA diastereomers 2, 3, 5, 6, 7, 9, 11, 13 and 14 (group 1) are degraded according
173 to first order kinetics, whereas the other five DFAs (1, 4, 8, 10 and 12) follow a different path
174 imposed by second-order kinetics (group 2). This difference is related to the chemical
175 structure and thermal stability of the compounds.

176 The DFAs present in the synthesized caramels studied here belong mostly to group 1 (about
177 70%). Consequently, a first-order kinetic was considered for the consumption of the set of
178 DFAs (path C). Four different configurations (Configurations I-IV) are proposed here to
179 determine the reaction orders of pathways A and B. In fact, several authors who have studied
180 the degradation of fructose in an acid medium observed first order kinetics for the formation
181 of HMF³⁰ and second order kinetics for the formation of acids.³¹ In the present study, the
182 reaction order and kinetic parameters were determined using the Polymath software to solve
183 the system equations 1 and 2, in which α is the partial reaction order of path A and β the
184 partial reaction order of path B. All the configurations were tested for the values of α and β .

185 $v_{Fructose} = -k_a [Fructose]^{\alpha} - k_b [Fructose]^{\beta}$ Equation 1

186 $v_{DFAs} = k_a [Fructose]^{\alpha} - k_c [DFAs]$ Equation 2

187 The configurations were evaluated by imposing values of k_a , k_b and k_c in order to adapt the
188 model to the experimental data of the reference test. The coefficients k_a , k_b and k_c were
189 determined by a two-step iterative method. The first step was to dichotomize the values of the
190 pair (k_a , k_b) to monitor the consumption of fructose. The value of k_c remained constant and
191 was set to 10^{-10} s^{-1} such that path C could be neglected in a first instance. In the second step,
192 the glycosylation reaction of DFAs (path C) was considered, changing the value of k_c . The
193 Polymath software represents the results in a graphical form (Figure 3).

194 The mechanism proposed by Configuration I fit the experimental data for the formation and
195 degradation of DFAs. In the case of fructose consumption, however, some divergences
196 between experimental and modeled results were observed. Up to 40 minutes, the model
197 followed the experimental points. However, after 60 min, a discrepancy was observed
198 between the experimental data and the model.

199 Whatever the k_c value, the results of Configuration II were inappropriate because the
200 theoretical amount of DFAs remained close to zero. In this configuration, the pathway B is
201 predominant; consequently the model does not generate enough DFAs to fit the experimental
202 points.

203 Modeling by III and IV configurations showed that fructose is primarily consumed to form
204 DFAs. The representation of the two configurations is therefore close at this temperature as
205 shown in Figure 3. Under these conditions, in both configurations the mechanism can be
206 limited by the DFA formation (pathway A) and consequently by the DFA consumption
207 (pathway C). The pathway B has a minimal influence on the fructose consumption. At this
208 stage, the reaction order of pathway B cannot be defined. Consequently, these two models
209 were applied to a new test carried out at 80 °C with a fructose ratio of 0.9 and a resin quantity

210 of 0.18 w/w_{mixture} to measure pathway B. Figure 4 shows that the best correlation coefficient
211 was obtained with configuration IV ($R^2 = 0.96$ for DFAs). This configuration proposes a
212 second order fructose consumption kinetics and a second order DFA consumption.

213 The kinetic parameter values for all the configurations are reported in Table 2. Therefore, the
214 kinetic equations are:

$$215 \quad v_{Fructose} = -k_a [Fructose]^2 - k_b [Fructose]^2 \quad \text{Equation 3}$$

$$216 \quad v_{DFAs} = k_a [Fructose]^2 - k_c [DFAs] \quad \text{Equation 4}$$

217 with v in $\text{g mL}^{-1} \text{ s}^{-1}$; k_a and k_b in $\text{mL g}^{-1} \text{ s}^{-1}$; k_c in s^{-1} and concentration in g mL^{-1} . Each kinetic
218 coefficient is dependent on temperature and resin concentration.

219 It should be noted that the predominant pathway is pathway A, which corresponds to the
220 formation of DFAs. For the reference experiment, the latter is even the only pathway.

221

222 **Effect of operational parameters on fructose consumption and DFA production**

223 The next aim was to study the effects of the operational parameters, including the initial
224 fructose mass fraction, the temperature and the resin catalyst loading, on the caramelization
225 reaction outcome and to obtain the kinetic parameters in order to characterize an optimal
226 process for the synthesis of prebiotic caramels (Figure 5).

227

228 **Fructose mass fraction effect**

229 A first set of experiments show the influence of the fructose mass fraction on the rate of
230 fructose consumption and DFA production. At the same temperature (90°C) and for different
231 fructose mass fractions (0.9, 0.8, 0.7), the kinetic coefficients are approximately constant. For
232 k_a , average of (4.5×10^{-4} ; 4.7×10^{-4} ; 4.7×10^{-4}) = $4.6 \times 10^{-4} \pm 0.12 \times 10^{-5}$. For k_b , the three values
233 are 1×10^{-4} . For k_c , average of (0.007; 0.014; 0.017) = 0.013 ± 0.005 . The results for k_c have
234 been found to be acceptable.

235 The experiment at 0.7 mass fraction shows that fructose conversion is lower than in the other
236 two cases (67% versus 80%). In addition, this experiment does not show an adequate fit to the
237 model (Figure 5a). Transfer phenomena could be modified with the fructose mass fraction.
238 The viscosity measurements show a significant decline which could explain this change in
239 kinetic behavior (337 mPa s for 0.7 and 3920 mPa s for 0.9 at 70 °C). Figure 5b shows that
240 the optimum DFA production is higher for the 0.9 mass fraction compared to the other
241 proportions (48% for the mass fraction of 0.9, 43% for the mass fraction of 0.8 and 38% for
242 mass fraction of 0.7). A fructose-rich medium promotes the production of DFAs.

243

244 **Temperature effect**

245 An increase in temperature favors the rate of fructose consumption (Figure 5c). Moreover,
246 Table 3 shows that kinetic coefficient decreases when the temperature decreases. At a
247 temperature of 90 °C, fructose consumption is controlled by the pathway that favors the
248 production of DFAs (Table 3). At 70 and 80 °C, the influence of pathway B is no longer
249 insignificant, since half of the fructose is consumed by the formation of HMF and
250 melanoidins. The DFA content is therefore much lower. Pathway C is favored with an
251 increasing temperature. DFA formation (Figure 5d) and reaction times are shorter as the
252 temperature increases (maximum DFA production: 32% at 120 min, 44% at 60 min and 48%
253 at 45 min at 70, 80 and 90 °C). In fact, at higher temperatures molecular agitation is promoted
254 and the viscosity of the mixture decreases. These two phenomena allowed a better transfer
255 between the solid phase and the liquid phase.

256 The rate constants of DFA formation (k_a), HMF and other products' formation (k_b) and DFA
257 consumption (k_c), at different temperatures, were applied to the Arrhenius plot. The resulting
258 equations are:

$$259 \quad k_a = k_{a,0} \times \exp(-96381/RT) \quad \text{Equation 5}$$

260 $k_b = k_{b,0} \times \exp(-29021/RT)$ Equation 6

261 $k_c = k_{c,0} \times \exp(-340485/RT)$ Equation 7

262 where R is the ideal gas constant (8.3144598 J mol⁻¹ K⁻¹), T is the temperature (K) and $k_{a,0}$,
263 $k_{b,0}$ et $k_{c,0}$ are the Arrhenius pre-exponential factors ($k_{a,0} = 3.27 \times 10^{10}$ mL g⁻¹ s⁻¹, $k_{b,0} = 2.11$ mL
264 g⁻¹ s⁻¹ et $k_{c,0} = 9.69 \times 10^{46}$ s⁻¹).

265 An activation energy value of 96 kJ mol⁻¹ is obtained for the formation of DFA (pathway A).
266 This value was higher to the one given by Chu and Berglund¹¹ (52 kJ mol⁻¹). On the other
267 hand, this value is in agreement with those obtained by Pazur³³, ranging from 85 to 165 kJ
268 mol⁻¹.

269 For HMF and other products formation (pathway B), the activation energy value is 29 kJ mol⁻¹
270 and is comparable to those obtained by Zhang et al.³⁴ (from 15 to 29 kJ mol⁻¹). However,
271 other authors^{35,36} talk about higher activation energies values between 120 and 150 kJ mol⁻¹.

272 Concerning DFA degradation into oligosaccharides (pathway C), an activation energy value
273 of 340 kJ mol⁻¹ is obtained but comparison with other authors is difficult due to a lack of
274 publication of this subject.

275

276 **Resin quantity effect**

277 The total rate of fructose consumption is decreased by a factor of two when comparing the
278 results obtained for 0.09 w/w_{mixture} and 0.27 w/w_{mixture} (Figure 5e). These values take into
279 consideration of fructose consumed by the pathway A and consumed by the pathway B. The
280 calculated coefficients $k_a + k_b$ are 6.3 10⁻⁴ mL g⁻¹ s⁻¹ and 3.0 10⁻⁴ mL g⁻¹ s⁻¹ respectively for
281 0.09 w/w_{mixture} and 0.27 w/w_{mixture} (Table 3). The results of Figure 5f show that the production
282 of DFAs is also variable when the percentage of resin increases. This trend can be attributed
283 to the decrease in pH in the medium, linked to a higher presence of acid catalyst. According
284 to the study by Chu and Berglund¹¹, an increase in pH decreases DFA production.

285 Nevertheless, DFA decrease can be also explained by a transfer problem. The ion exchange
286 resin effectively reduces the reaction time by progressively releasing the cation for activation
287 of the caramelization as determined by Suarez-Pereira (2010). However, as the percentage of
288 resin increases, viscosity increases causing diffusion problems and consequently decreased
289 reactivity. The medium becomes doughy and more difficult to agitate and homogenize in
290 relation of resin content. A viscosity study was conducted and shows, for example, that in
291 90% fructose syrup at 90°C, the viscosity is equal to 760 mPa s for 0.18 g resin/g mixture and
292 reach to 1030 mPa s for 0.27. Lastly, the high viscosity reduces the production of fructosyl-
293 DFAs and fructo-oligosaccharides. The k_c values are 0.015 s^{-1} , 0.007 s^{-1} and 0.006 s^{-1} for resin
294 proportions of 0.09, 0.18 and 0.27 w/w_{mixture}, respectively.

295

296 CONCLUSION

297 The model proposed to describe fructose consumption is based on a second-order global
298 kinetic model: a pathway for the generation of by-products such as HMF, formic acid, and
299 lactic acid and a pathway for the production of DFAs. The evolution of DFAs is modeled by
300 two successive reactions: DFA production (second order reaction) and DFA consumption
301 (first order reaction). The second reaction was determined from the DFAs generated during
302 kinetics. This model provides a qualitative understanding of the phenomena that occur and a
303 quantitative description of these processes. This set was evaluated by calculating the kinetic
304 coefficients. Although it cannot provide a complete quantitative description, this model gives
305 reliable information on the simplified caramelization process operating under the investigated
306 heterogeneous conditions. In this work, the by-product pathway may be insignificant
307 compared to DFA production. Finally, favorable conditions for obtaining caramel enriched in
308 di-D-fructose dianhydride (about 50%) were identified, namely a high fructose proportion
309 (0.9), high temperature (90 °C) and a resin proportion of 0.18 w/w_{mixture}.

310

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412

413 **TABLES**

414

415 Table 1: Fructose conversion and DFA production for caramels prepared with new resin, resin

416 regenerate one time and resin regenerate two time.

	Fructose conversion ratio (%) at 120 min	DFA maximum production (%) (at different time)
new resin	88	30 (55 min)
resin regenerate one time	86	20 (120 min)
resin regenerate two time	39	15 (120 min)

417

418

419

420 Table 2. Kinetic coefficients calculate by Polymath.

Conditions	Parameters	Configurations			
		I $\alpha = 1; \beta = 1$	II $\alpha = 1; \beta = 2$	III $\alpha = 2; \beta = 1$	IV $\alpha = 2; \beta = 2$
fructose: 0.9 resin: 0.18 w/w T: 90 °C	k_a	$3 \times 10^{-3} \text{ s}^{-1}$	$3 \times 10^{-3} \text{ s}^{-1}$	$4.5 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$	$4.5 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$
	k_b	$1 \times 10^{-6} \text{ s}^{-1}$	$0.4 \times 10^{-3} \text{ mL g}^{-1} \text{ s}^{-1}$	$1 \times 10^{-10} \text{ s}^{-1}$	$1.4 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$
	k_c	0.015 s^{-1}	-	0.012 s^{-1}	0.007 s^{-1}
fructose: 0.9 resin: 0.18 w/w T: 80 °C	k_a	-	-	$3 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$	$1.8 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$
	k_b	-	-	$7 \times 10^{-10} \text{ s}^{-1}$	$1.1 \times 10^{-4} \text{ mL g}^{-1} \text{ s}^{-1}$
	k_c	-	-	0.009 s^{-1}	$9 \times 10^{-4} \text{ s}^{-1}$

421

422

423 Table 3. Effect of operational parameters on kinetic coefficients.

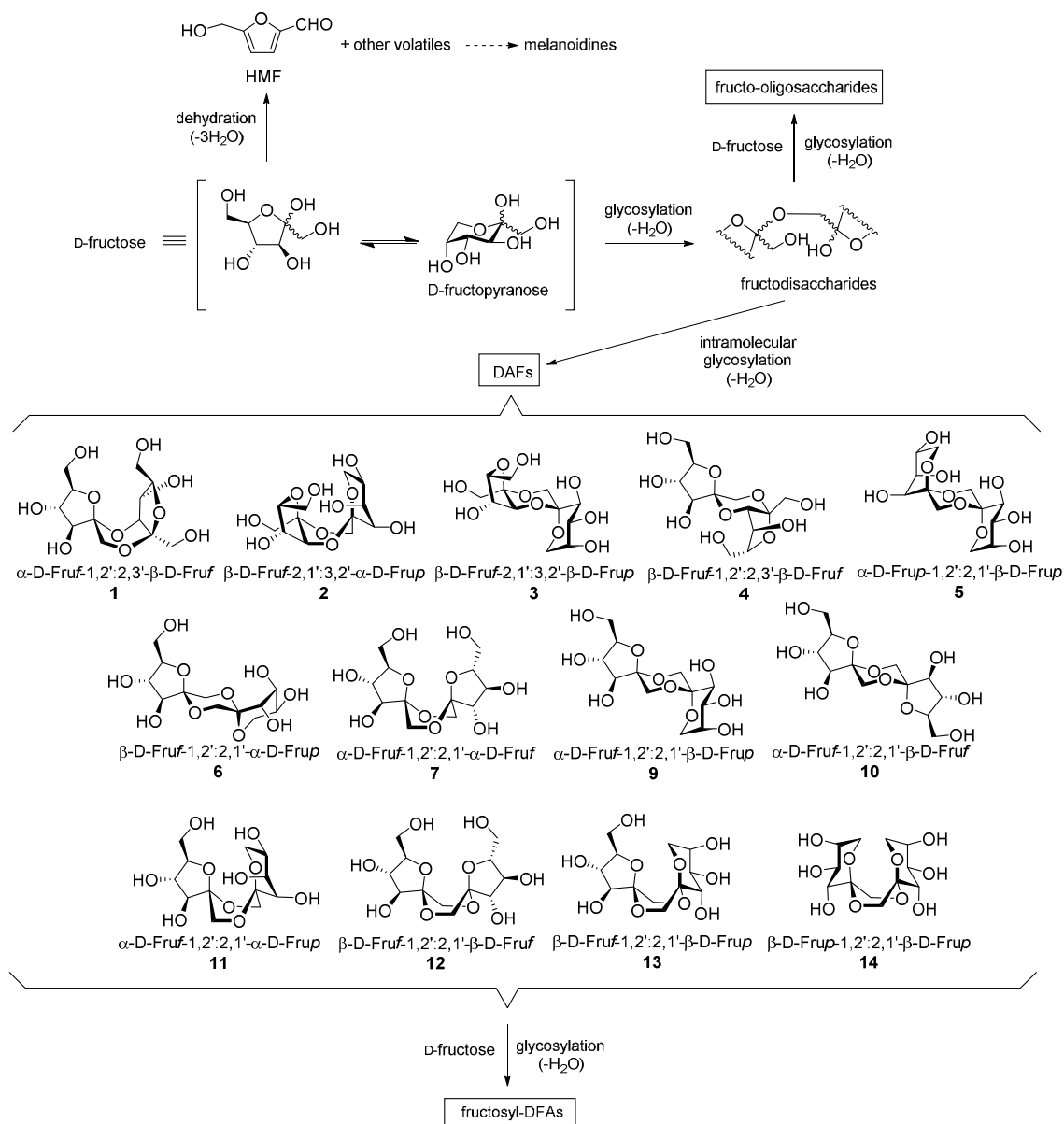
Conditions		k_a [mL g ⁻¹ s ⁻¹]	k_b [mL g ⁻¹ s ⁻¹]	k_c [s ⁻¹]	
fructose mass fraction effect	T: 90 °C resin: 0.18 w/w	0.9	4.5×10^{-4}	1.4×10^{-4}	0.007
		0.8	4.7×10^{-4}	1×10^{-4}	0.014
		0.7	4.7×10^{-4}	1×10^{-4}	0.017
temperature effect	fructose: 0.9 resin: 0.18 w/w	90 °C	4.5×10^{-4}	1.4×10^{-4}	0.007
		80 °C	1.8×10^{-4}	1.1×10^{-4}	0.0009
		70 °C	0.7×10^{-4}	0.8×10^{-4}	0.00001
resin quantity effect	fructose: 0.9 T: 90 °C	0.09 w/w _{mixture}	5×10^{-4}	1.3×10^{-4}	0.015
		0.18 w/w _{mixture}	4.5×10^{-4}	1.4×10^{-4}	0.007
		0.27 w/w _{mixture}	2.3×10^{-4}	0.7×10^{-4}	0.006

424

425

426 **FIGURE GRAPHICS**

427



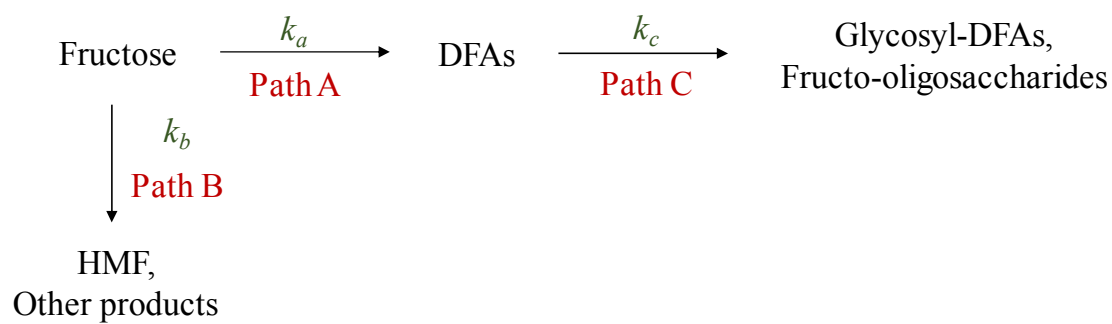
428

429 Figure 1. Main transformations occurring during the caramelization of D-fructose and

430 chemical structure of the di-D-fructose dianhydrides with indication of the intersaccharide

431 glycosidic bonds, the anomeric configuration (α or β) and the cyclic form of the fructose units432 (*f*, furanose; *p*, pyranose).

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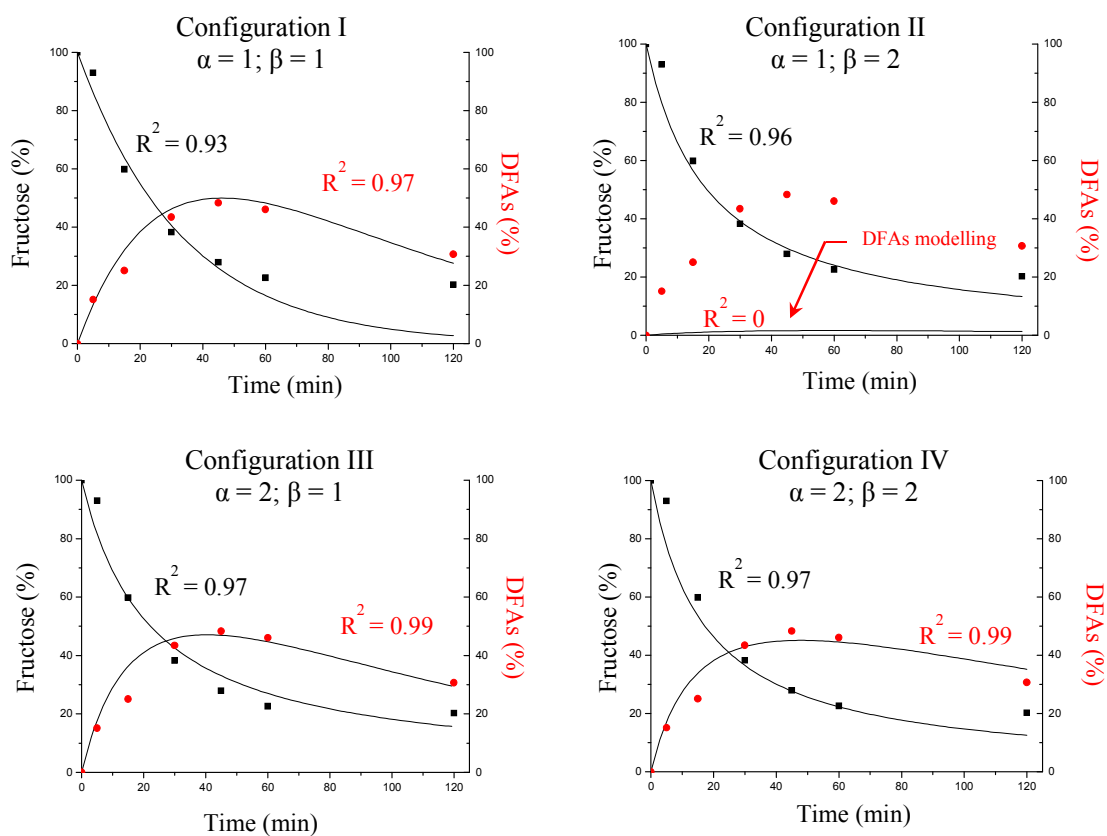


434

435 Figure 2. Simplified mechanism of fructose transformation.

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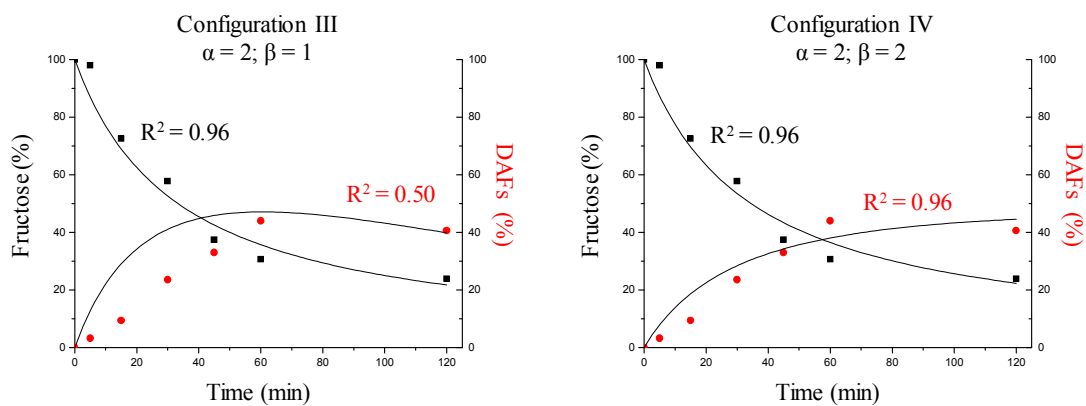
438

439 Figure 3. Modeling of the reference experiment (fructose mass fraction of 0.9, water mass

440 fraction of 0.1, temperature of 90 °C and resin quantity of 0.18 w/w_{mixture}).

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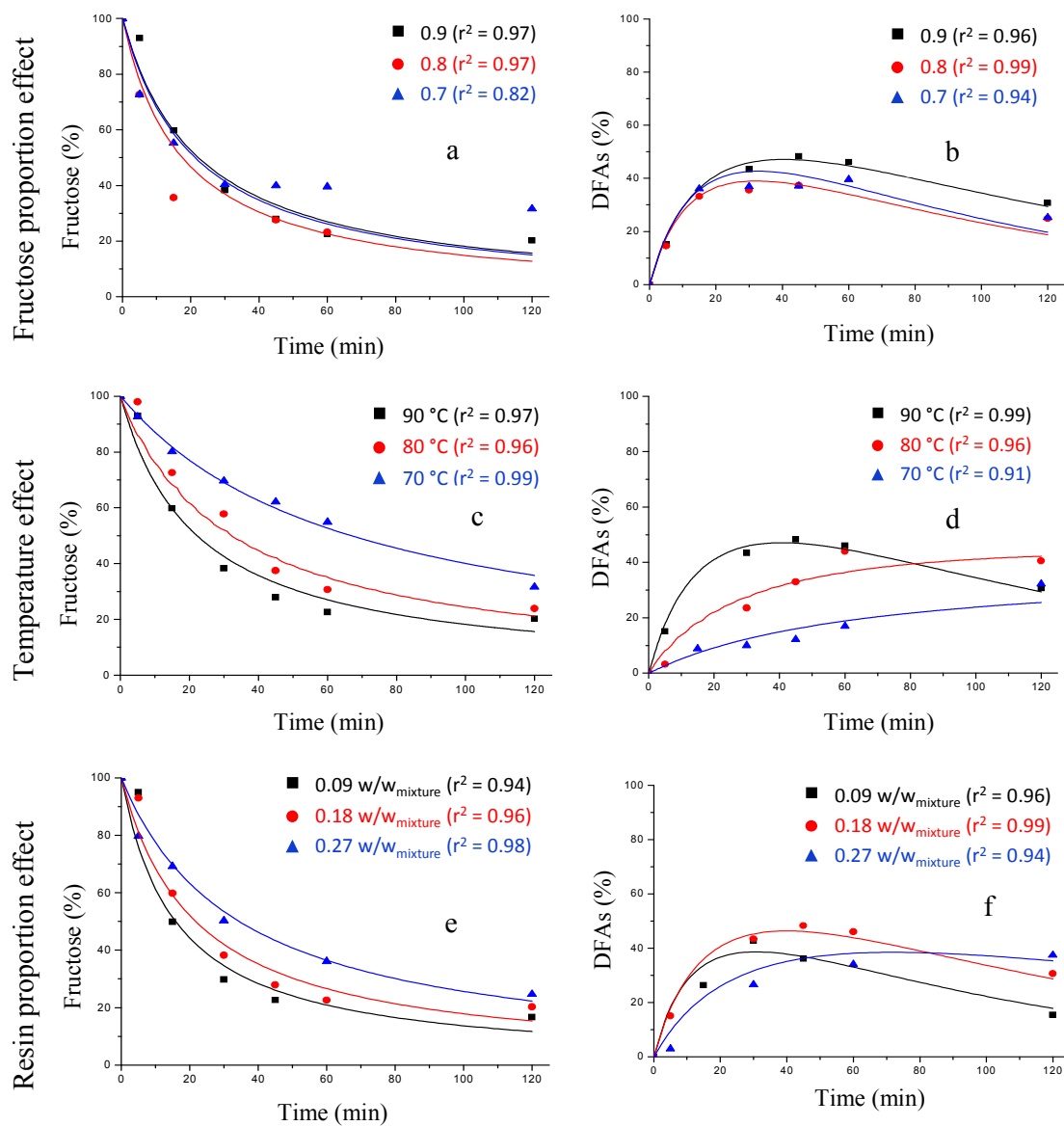


443

444 Figure 4. Evolution of the amounts of fructose and DFAs as a function of time (fructose mass
445 fraction of 0.9, water mass fraction of 0.1, temperature of 80 °C and resin quantity of 0.18
446 w/w_{mixture}).

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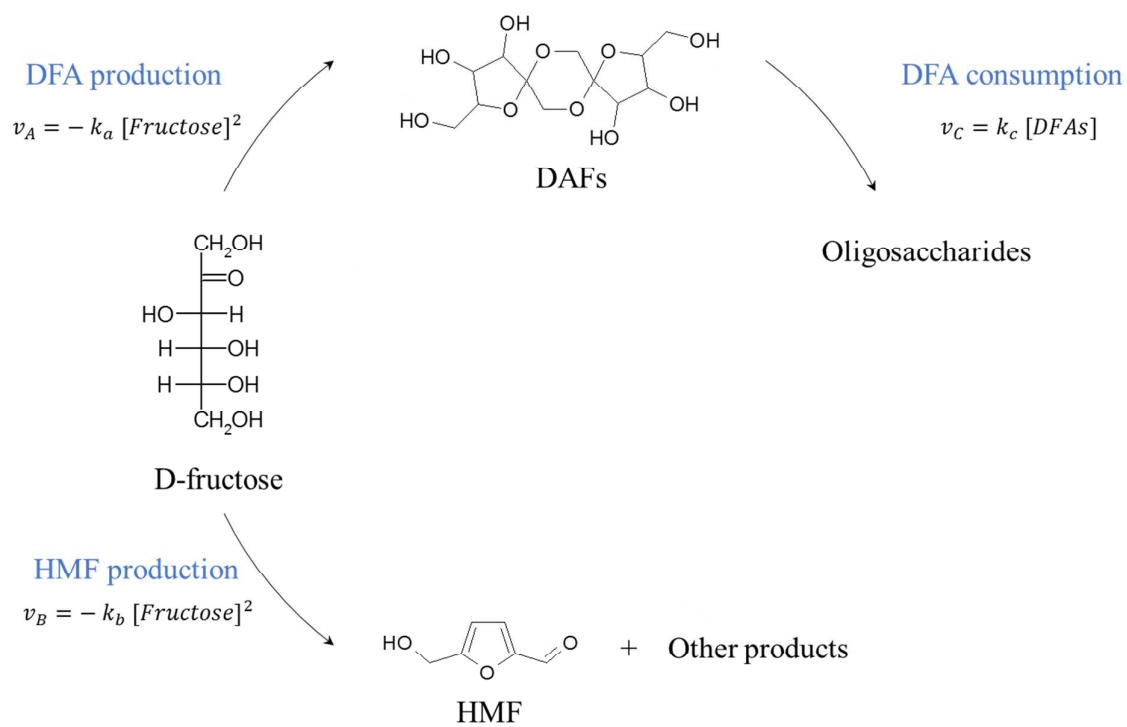
449

450 Figure 5. Effect of operational parameters on fructose consumption and DFA production

451 (reference conditions: fructose mass fraction of 0.9, water mass fraction of 0.1, temperature of

452 90 °C and resin quantity of 0.18 w/w_{mixture}).

453

454 **TOC graphic**

455

456