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# 1 Role of solvent the production of butyl levulinate from fructose

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10 **Abstract:** The use of alkyl levulinates is growing interest in fuels. Adding n-butyl levulinate (BL) to fuels  
11 presents some benefits compared to ethyl levulinate. The conventional production route of BL is from  
12 the esterification of levulinic acid, but the latter compound presents some corrosion issues. Alcoholysis  
13 of fructose by butanol over cation exchange resins (solid catalyst) seems to be a better alternative. The  
14 effect of water addition, solvent, swelling effect (from the cation exchange resin), and fructose solubility  
15 at temperatures higher than 25°C are unclear on this reaction. To understand these effects, the  
16 alcoholysis of fructose by butanol at 110°C in different solvents, e.g., gamma-valerolactone (GVL), were  
17 studied in a pressurized autoclave in an inert environment. The dissolution study was conducted in a  
18 temperature range of 20-120°C in different solvents. The concentration profiles of fructose, 5-  
19 (hydroxymethyl)furfural (HMF), 5-(butoxymethyl)furfural (BMF) and BL were analyzed in different  
20 solvents: butanol/water, butanol, butanol/GVL/water and butanol/GVL. We found that using a  
21 butanol/GVL (70/30 wt%) solvent is better from the conversion and dissolution viewpoints.

22 **Keywords:** Mass transfer; Alcoholysis; Solvent effect; Solid catalyst

23

24 1. Introduction

25 The depletion of fossil fuels together with growing concern about the environmental impact of human  
26 activities is pushing the research for new and renewable sources of energy and raw materials.  
27 Lignocellulosic biomass (LCB) is considered a valuable ally in producing chemicals, fuels, and materials,  
28 being an abundant, renewable and carbon-fixing resource. In opposition to food biomass which can  
29 incur in the food versus fuel dilemma, LCB (second generation biomass) represents an excellent  
30 alternative feedstock in biorefinery [1,2]. In this context, the use of lignocellulosic biomass and its  
31 conversion to value-added chemicals and fuels has become increasingly widespread. [3,4]. Considering  
32 LCB main components: lignin, cellulose and hemicellulose, the development of lignin valorization into  
33 chemicals is still under progress due to its complex and heterogeneous aromatic polymeric structure [5–  
34 11]. Meanwhile, the industrial valorization of cellulose and hemicellulose into so-called platform  
35 molecules is mature [12–18]. Several pretreatments allow fractionating these complex biomass polymers  
36 into simple sugar-monomers, valuable through different chemical pathways to several platform  
37 molecules such as 5-(Hydroxymethyl)furfural (HMF), glycols, sorbitol or levulinic acid and alkyl  
38 levulinates (Fig. 1) [17–19].

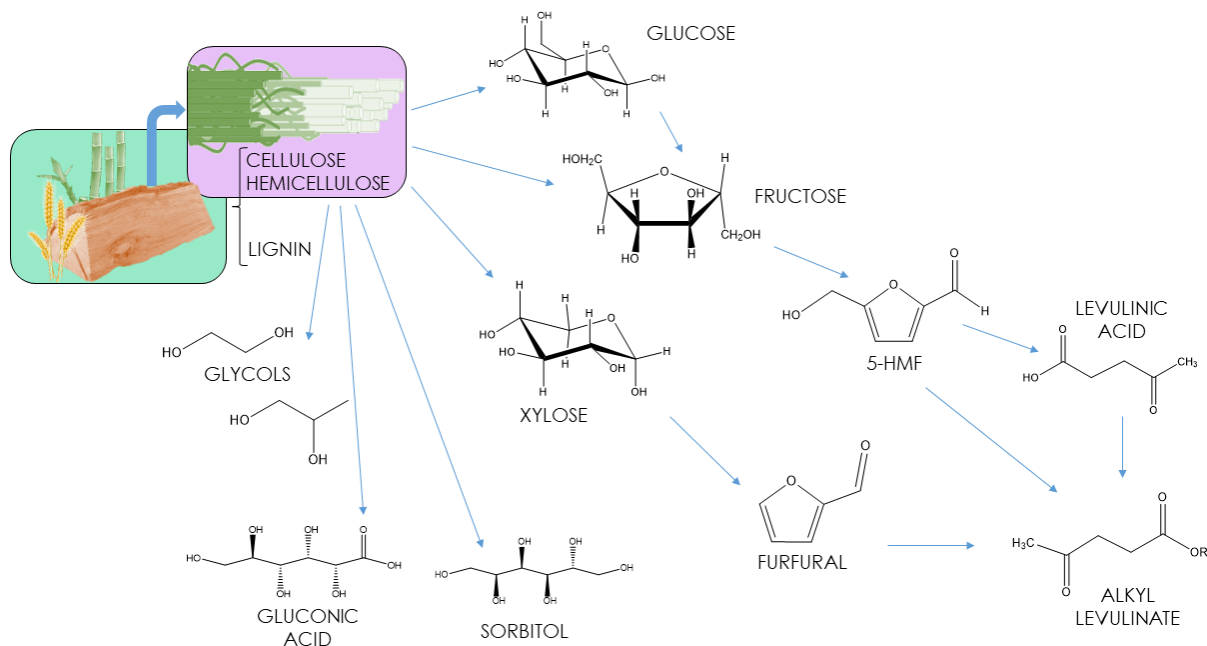


Fig. 1. Valorization of cellulose adapted from literature [18].

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42 Alkyl levulinates are promising and versatile platform molecules issued from cellulose and/or  
43 hemicellulose alcoholysis with broad industrial applications. Esters of levulinic acid can simply be  
44 produced by esterification of levulinic acid [20–23], but the low yield in the production of levulinic acid,  
45 together with the high costs of separation and purification, make this route less beneficial compared to  
46 using more affordable starting feedstocks as biomass-derived monosaccharides: glucose and fructose  
47 [4,24–31]. Although glucose is the most abundant monomers and the least expensive substrate over  
48 other monomers [32], fructose shows higher molecular instability and faster reactivity to be dehydrated  
49 to 5-(hydroxymethyl)furfural, first intermediate in the pathway to alkyl levulinate, whereas glucose must  
50 first be isomerized to fructose [33].

51 From an energy viewpoint, alkyl levulinates can be used as blending components for biodiesel or fuel  
52 oxygenate additives [34,35], improving fuel quality and reducing pollutant emission [36,37]. In 2017,  
53 Tian et al. demonstrated that methyl and ethyl levulinate have higher anti-knock quality than Euro95  
54 gasoline [38]. Wang et al. investigated the use of ethyl levulinate as a diesel blend, resulting in a higher  
55 closed cup flash point, oxygen content, and lower kinematic viscosity compared to n-butanol [39].  
56 Christensen et al., have shown that butyl levulinate (BL) can improve conductivity, cold flow properties  
57 and lubricity of diesel fuel and reduce its vapor pressure [40]. Furthermore, BL was found to remain in  
58 solution with diesel down to the fuel cloud point and to have more compatibility with elastomers,  
59 compared to ethyl levulinate, which tends to separate from diesel at a temperature below 0 °C and  
60 results to be more corrosive [40]. Frigo et al. showed that diesel fuel blended with a mixture of butyl  
61 levulinate and dibutyl ether could reduce particulate emissions without changing engine power efficiency  
62 or increasing the NO<sub>x</sub> emission [41].

63 Alcoholysis of sugar monomers to BL is catalyzed mainly by Brønsted-acids [42]. Traditional mineral  
64 acids are gradually being substituted by heterogeneous acid catalysts, cause of equipment corrosion,  
65 separation and neutralization costs. Zeolites, ion exchange resins, metal oxides, nanomaterials and  
66 other numerous solid catalysts have been tested to produce butyl levulinate from biomass-derived  
67 carbohydrates [42].

68 An et al. studied the production of BL from the alcoholysis of different carbohydrates and found that  
69 ferric sulfate was the most efficient [33]. They found that with a catalyst loading of 5 g/L, a reaction  
70 temperature of 190°C, and a fructose concentration of 25 g/L, the yield of BL was found to be 62.8 mol%  
71 for 3 hours of reaction time.

72 Higher alkyl levulinate yields from fructose were also confirmed by Liu et al. [29] using sulfonic acid-  
73 functionalized carbon materials. BL has been produced with a yield of 78 mol% after 12 h and complete  
74 fructose conversion [29].

75 Ramirez et al. made an in-depth assessment on the use of ion-exchange resins for the direct  
76 transformation of fructose into BL by alcoholysis [43]. Using a water/butanol mixture, they detected BL  
77 production only at a temperature higher than 100°C. They also showed that between 17-37% of fructose  
78 is lost in humins production. They studied catalyst reuse and found that fresh and twice-reused catalysts  
79 have similar activity. In this assessment, gel-type Dowex 50Wx2 resulted in the best catalyst according  
80 to BL yield.

81 Several research studies on the alcoholysis of sugars into alkyl levulinate essentially focus on the  
82 catalysis. To the best of our knowledge, there are not many studies on the crucial role of solvent, which  
83 can affect the reaction kinetics and the product selectivity, sugar dissolution, polymerization, and  
84 degradation. Sun et al. reported that the conversion of sugars and furans, particularly fructose and 5-  
85 (hydroxymethyl)furfural, is different in different solvents, depending on their polarity and protic aprotic  
86 nature [44]. Protons transfer is a key point in the acid-catalyzed alcoholysis mechanism, and the solvent  
87 plays a crucial role [45]. Sugar monomers showed high reactivity in water, one of the most used solvents  
88 in lignocellulosic biomass derivatives pretreatment and conversion. Water provides a good solvation  
89 environment, allowing high dissociation of Brønsted acids and also high solubility of carbohydrates [46].  
90 On the other hand, the high reactivity in aqueous systems results in greater instability of sugars and  
91 furan intermediates which tend to undergo acid-catalyzed side reactions, as production of by-product  
92 humins [44,47,48]. An alternative to minimize side reactions is using polar organic solvents, particularly  
93 alcohols [47,48]. Some studies reported promising alkyl levulinates yields from fructose alcoholysis in  
94 pure alcohols. Ramirez et al. [43] obtained a 73.4 mol% butyl levulinate yield from fructose alcoholysis  
95 in pure butanol, and Sun et al. [44] a yield of 51.6 mol% ethyl levulinate from fructose alcoholysis in pure  
96 ethanol, both catalyzed by ion exchange resins. Excess of alcohol results in a major control of the  
97 conversion steps, protons transfer and limitation of the polymerization of sugars and furans [44,46]. In  
98 pure butanol solvent, the selectivity of BL can also be lowered by the side reaction of etherification  
99 producing dibutyl ether [43,49,50]. Besides the polar protic alcoholic medium, some studies highlighted  
100 the role of polar aprotic solvents in lowering unwanted degradation reactions of intermediates [51,52].  
101 The introduction of co-solvents might further minimize possible side-reaction products. Among polar  
102 aprotic solvents,  $\gamma$ -valerolactone (GVL) may be a valid co-solvent in fructose alcoholysis. Several

103 patents suggested it as a green alternative to classical hazardous solvents since it can be produced  
104 starting from derived-biomass fructose via hydrogenation of levulinic acid or alkyl levulinates [53]. In  
105 2014, M.A. Mellmer et al. [52] demonstrated the benefits of using polar aprotic solvents, such as GVL,  
106 for acid-catalyzed reactions. Capecchi et al. [54] reported the synthesis of GVL by hydrogenation of butyl  
107 levulinate, identifying an excess of GVL as the best solvent system. Although the REACH registration is  
108 still missing for GVL, some acute toxic data ( $LD_{50}$  oral-rat = 8800 mg/kg), its overall structure and  
109 properties suggest its stability, biodegradability and not toxicity [55], responding to the principle of benign  
110 solvents and auxiliaries of Green Chemistry principles [56].

111 Despite many publications on this topic, several aspects are missing in the literature concerning the  
112 alcoholysis of fructose over cation exchange resins, such as the solvent effect, the role of water, the  
113 resin swelling and fructose dissolution within a temperature range of 60-100°C. In this study, a deep  
114 investigation on the production of BL from the fructose alcoholysis was carried out over an ion exchange  
115 resin: Amberlite IR-120. Being very effective in sugar monomers conversion and esterification reactions  
116 [57–60], Amberlite IR-120 was chosen because of its good stability, high proton capacity, affordability  
117 and recyclability without a significant decrease in its activity [58,61,62]. Solvent effects on the production  
118 of BL and intermediates were evaluated as well as on the fructose dissolution at different temperatures.  
119 A mass transfer study was performed, and the swelling of Amberlite IR-120 was also measured

120

121 2. Experimental section

122 2.1 Chemicals

123 Fructose ( $\geq 99\%$  purity), 5-(hydroxymethyl)furfural (HMF, 99% purity), 5-(ethoxymethyl)furfural (EMF,  
124 97% purity) and  $\gamma$ -valerolactone ( $\geq 99\%$  purity) were purchased from Sigma-Aldrich.  
125 1-Butanol (BuOH,  $\geq 99,5\%$  purity), butyl levulinate (BL,  $\geq 98\%$  purity), acetonitrile (ACN,  $\geq 99,9\%$  purity),  
126 butyl formate (BF,  $\geq 97\%$  purity) and acetone ( $\geq 99,9\%$  purity) from VWR chemicals. Amberlite IR120  
127 ( $H^+$  form, ion-exchange resin) commercial catalyst provided by Acros Organics. Nitrogen gas ( $N_2$  purity  
128  $> 99,999$  vol%) from Linde. All chemicals were employed without further purification.

129 2.2 Analytical methods

130 Reaction samples were analyzed by combining gas and liquid chromatography. HPLC Agilent 1100  
131 Series was employed to quantify fructose, equipped with a SUPELCO SIL LC-NH<sub>2</sub> column (250 mm x  
132 4.6 mm x 5  $\mu$ m), a UV detector set at 191 nm, and by using a mixture of acetonitrile and ultrapure water  
133 (90:10 v/v %) as mobile phase, with a flow rate of 1 mL/min and constant column temperature of 30 °C.  
134 Reaction products, such as HMF, BL, 5-(butoxymethyl)furfural (BMF), and solvent systems were  
135 detected by Bruker Scion 456-GC, equipped with a VF-1701ms Agilent column (60.0 m x 250  $\mu$ m x 0.25  
136  $\mu$ m) and a flame ionization detector (FID). The injector and detector temperature were 250 °C, and the  
137 oven temperature was programmed from 40 °C to 250 °C with 20 °C/min of ramp rate. All experimental  
138 quantifications were based on daily calibration curves with standard solutions of pure commercially  
139 available chemicals. EMF was used as a reference for the BMF calibration curve due to its commercial  
140 unavailability. Each experimental sample was analysed three times to estimate the error in the analytical  
141 method, in term of standard deviation.

142 Fructose conversion, butyl levulinate yield and catalyst loading were defined as follows:

143 Fructose conversion (%) =  $\left(1 - \frac{\text{mole of fructose after the reaction}}{\text{initial mole of fructose}}\right) * 100$  (1)

144 BL yield (%) =  $\frac{\text{mole of BL after the reaction}}{\text{initial mole of fructose}} * 100$  (2)

145 Catalyst loading ( $\omega_{CAT}$ ) =  $\frac{\text{mass of catalyst}}{\text{liquid volume}}$  (g/L) (3)

146

147 2.3 Experimental set-up

148 The alcoholysis reaction runs were performed in a 300 mL Parr stainless steel batch reactor, under  
 149 isothermal and isobaric conditions. The reactor was equipped with an electrical heating jacket and a  
 150 cooling coil, together with a thermocouple capable of measuring the reaction temperature and  
 151 communicating with the temperature controller. The presence of a gas entrainment impeller (diameter  
 152 2.5 cm) with a hollow shaft provided a uniform mixing of the reacting mixture.

153 For each experiment, the reactor was loaded with 1.6 g of fructose, 35 g/L of catalyst loading (4.5 – 4.9  
 154 g of catalyst) and a fixed volume of liquid. After loading the reaction mixture, catalyst and assembling  
 155 the reactor, the system was pressurized with nitrogen at 20 bars to limit the gas-liquid partition of the  
 156 liquid phase [43,58]. Then, the temperature heater and rotation stirrer were switched on. The first sample  
 157 was collected when the desired temperature was reached (time zero). Following the time zero sample,  
 158 samples were collected at 5 min, 30 min, and then every hour up to 7 h. The reaction temperature was  
 159 fixed to 110 °C, demonstrated by preliminary experiments to be the optimum between catalytic activity  
 160 and catalyst resistance towards temperature. Indeed, sulfonic groups, i.e., active sites, from Amberlite  
 161 IR-120 can leach when the temperature is higher than 120°C. Table 1 shows the experimental matrix  
 162 with the different solvent systems.

163 Table 1: Experimental matrix with the initial amount of fructose, butanol, water and GVL.

	Run	Fructose (g)	Butanol wt%	Water wt%	GVL wt%	$\omega_{\text{CAT}}$ (g/L)	T(°C)	rpm	Reaction time (h)	Inert gas
<b>No GVL</b>	1	1.6	83	17	0	35	110	800	7	N <sub>2</sub> (20 bar)
	2	1.6	91.5	8.5	0	35	110	800	7	N <sub>2</sub> (20 bar)
	3	1.6	96	4	0	35	110	800	7	N <sub>2</sub> (20 bar)
	4	1.6	100	0	0	35	110	800	7	N <sub>2</sub> (20 bar)
<b>GVL</b>	5	1.6	2.5	8.5	89	35	110	800	7	N <sub>2</sub> (20 bar)
	6	1.6	60.5	8.5	30	35	110	800	7	N <sub>2</sub> (20 bar)
	7	1.6	76.5	8.5	15	35	110	800	7	N <sub>2</sub> (20 bar)
	8	1.6	70	0	30	35	110	800	7	N <sub>2</sub> (20 bar)

164

165 Amberlite IR-120 was pre-treated before its use, as described by Leveneur et al. [62]. The catalyst was  
 166 washed through several cycles in water and a final one in butanol, which is the main reaction solvent,  
 167 after being dried in an oven at 90 °C at atmospheric pressure for 5 hours. Amberlite IR-120 is a cation  
 168 exchange resins composed of sulfonated styrene-divinyl benzene (PS-DVB) matrix with sulfonic acid  
 169 functional groups. The catalyst is a gel-type resin, bead-shaped, in which PS-DVB copolymers result in



170 a set of tangled chains with no spaces between them in the dry state. The degree of cross-linking, linked  
 171 to the level of divinylbenzene, represents the tightness of the resin. Table 2 shows the properties of  
 172 Amberlite IR-120.

173 Table 2: Properties of Amberlite IR-120 according to the manufacturer (Acros Oganics).

Supplier	Acros Organics
Structure	Styrene-divinylbenzene
Resin type	Gel-type
Cross linking (DVB%)	8
Moisture content (% mass)	48-58
Capacity by dry weight ( $m_{eq}/g$ )	4.4
Native particle size range ( $\mu m$ )	$\geq 94 \%$ ( $300 < d < 1180 \mu m$ )

174

175 2.4 Mass transfer study

176 To evaluate the effect of internal mass transfer, it is important to measure the effect of different particle  
 177 size ranges on the kinetics. Thus, the dried catalyst particles were sieved. As a result, the dried particle  
 178 size distribution (PSD) evidenced a high percentage (ca. 84 %) of particles with diameters higher than  
 179 500  $\mu m$  and the remaining particles with diameters between 300 and 500  $\mu m$ . The influence of external  
 180 and internal mass transfer resistances was investigated by varying agitation speed and particle size. As  
 181 shown in Table 3, varying the rotating speed between 500 and 1000 rpm, the external mass transfer  
 182 limitation was studied for the finest particle size distribution (runs 1',2',3' in Table 3). An optimum rotating  
 183 speed was selected to suppress the external mass transfer resistance. The presence of internal mass  
 184 limitation was examined by considering the different particle size distribution (finest, highest and native  
 185 distribution; Runs 4',5',6' in Table 3).

186 Table 3: Experimental matrix for external and internal mass transfer limitation investigations.

	RUN	PSD	Fructose (g)	Butanol wt%	Water wt%	$\omega_{CAT}$ (g/L)	T( $^{\circ}C$ )	rpm	t(h)	Inert gas
<b>Ext.</b>	1'	Fine	1.6	83	17	35	110	500	7	N <sub>2</sub> (20 bar)
	2'	Fine	1.6	83	17	35	110	800	7	N <sub>2</sub> (20 bar)
	3'	Fine	1.6	83	17	35	110	1000	7	N <sub>2</sub> (20 bar)
<b>Int.</b>	4'	Fine	1.6	83	17	35	110	800	7	N <sub>2</sub> (20 bar)
	5'	High	1.6	83	17	35	110	800	7	N <sub>2</sub> (20 bar)
	6'	Native	1.6	83	17	35	110	800	7	N <sub>2</sub> (20 bar)

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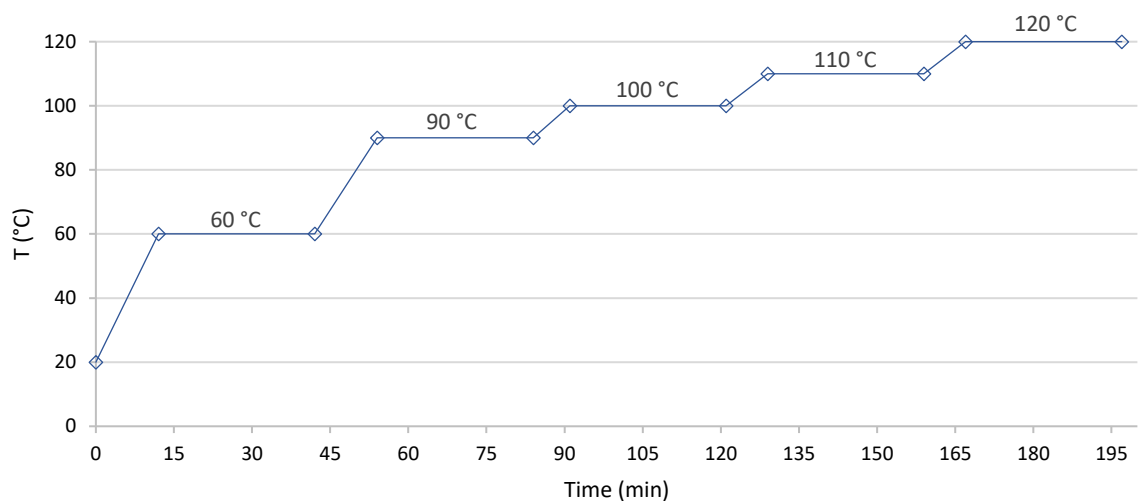
189 Being characterized by cross-linked styrene-divinylbenzene, the particle size of Amberlite IR120 is also  
190 affected by the swelling effect due to the solvent. In other words, even if the amount of dried catalyst is  
191 the same, the kinetics could be different if the solvent is different due to different swelling behavior. The  
192 same procedure described in the article of Russo et al. was used [58,63]. Based on the Bodamer and  
193 Kunin procedure [64], the swelling degree was investigated in each solvent system to observe the  
194 catalyst behavior in all solvents. The parameter was evaluated by adding an aliquot of 20 mL of dry  
195 catalyst to a graduated cylinder of 100 mL. The initial volume was read to the nearest 0.5 mL. Then, the  
196 resin was covered with the specific solvent mixture to fill the cylinder volume without shaking and  
197 tapping. After 120 h, the volume was read, and the swelling percentage was calculated as follows:

$$198 \quad \%SW = \frac{\text{final volume } (V_{\text{final}}) - \text{initial volume } (V_{\text{initial}})}{\text{initial volume } (V_{\text{initial}})} * 100 \quad (4)$$

199

## 200 2.5 Fructose dissolution investigation

201 The fructose dissolution has been measured in the different solvent mixtures considered in this study.  
202 By using the same experimental equipment described above, a modified analytical method was applied  
203 [65]; a solvent mixture of 140 mL volume together with a known amount of fructose (i.e. the specific  
204 fructose concentration of 11 g/L used in the alcoholysis experiments) is added to the system, kept in  
205 agitation at 800 rpm, at constant temperature and pressure and for a period of time sufficient to  
206 determine the equilibrium of the system. Engasser et al. [66] observed a rapid initial phase in the  
207 dissolution kinetics of fructose in which around 40% of the maximal concentration was reached in less  
208 than 5 minutes. Thus, a time interval of 30 min was assumed as sufficient to reach the equilibrium in  
209 this study. The system was tested under different temperature conditions by measuring the fructose  
210 concentration at each temperature (Fig. 2). In particular, fructose dissolution has been investigated in  
211 pure butanol and butanol-GVL mixture 70/30 wt% (Table 4).



212

213

Fig. 2. Temperature profile versus time in fructose dissolution study.

214

Table 4: Experimental matrix for fructose dissolution study.

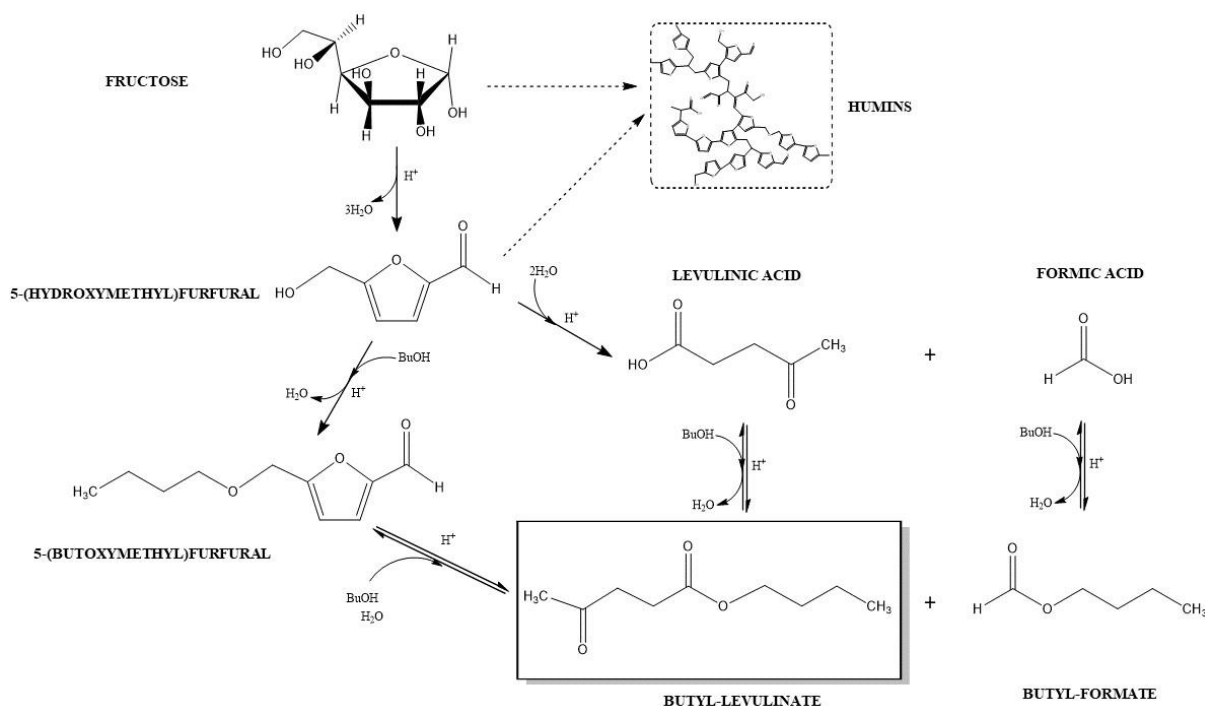
RUN	Fructose (g)	Butanol wt%	GVL wt%	rpm	Inert gas
S1	1.6	100	0	800	N <sub>2</sub> (20 bar)
S2	1.6	70	30	800	N <sub>2</sub> (20 bar)

215

216

217 3. Results and discussion

218 According to several articles, the reaction mechanism of fructose alcoholysis by butanol occurs  
 219 according to Fig. 3 [43,67–69]. In acidic system, fructose tends to be rapidly dehydrated to HMF, first  
 220 reaction intermediate. Through the alcoholic medium, HMF can be rehydrated to levulinic acid, then  
 221 esterified to butyl levulinate or be transformed into the corresponding ether, 5-BMF, then converted to  
 222 BL. Besides BL, butyl formate is also produced in an equimolar ratio. Experimentally, we observed the  
 223 pathway through 5-(butoxymethyl)furfural (HMF) as dominant since the production of levulinic acid is  
 224 very low, with concentrations close to zero throughout the reaction time. This might be due to the low  
 225 water concentration, which is insufficient to favor the rehydration of HMF rather than its etherification  
 226 with butanol [42]. For this reason, LA concentration trends were not considered in the subsequent  
 227 discussion of the results. Furthermore, the reaction scheme constituted of several consecutive and  
 228 parallel reactions also count the inevitable production of humins from polymerization side-reactions of  
 229 fructose and HMF. Studies claim that BMF does not degrade into humins [67].



230  
 231  
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 234  
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 236

Fig. 3. Reaction steps for the fructose alcoholysis in an acid-catalyzed system.

237 3.1 Swelling effect

238 Table 5 shows that the swelling test of Amberlite IR120 showed similar behavior in the different solvents  
 239 and mixtures tested: pure butanol, pure GVL, pure water, BuOH/GVL/Water, BuOH/GVL and  
 240 BuOH/Water. Although slightly lower in pure GVL, the swelling factor is over 100 % in each solvent  
 241 system. Hence, the difference of kinetics for the alcoholysis of fructose by butanol over Amberlite IR-  
 242 120 in these solvents is not due to the swelling effect. Therefore, if the swelling effect is the same in  
 243 these solvents, the mass transfer study was only performed in BuOH/Water.

244 Table 5: Results from swelling study of Amberlite IR-120 at room temperature.

Solvent		$V_0$ (mL)	$V_{fin}$ (mL)	%SW
Pure BuOH	-	20	42	110±5
Pure GVL	-	20	39	95±5
Pure Water	-	20	42	110±5
BuOH/GVL/Water	53/30/17 %wt	20	42	110±5
BuOH/GVL	70/30 %wt	20	42	110±5
BuOH/Water	83/17 %wt	20	41	105

245

246 While the results in pure water and binary mixture butanol-water are comparable with the ones obtained  
 247 in literature (around 100 % in water and 110 % in ethanol-water mixture) [58,64], the swelling effect in  
 248 pure butanol is higher than that reported in the literature for ethanol (40 % obtained by Bodamer and  
 249 Kunin [64], 70 % by Russo et al. [58]). The swelling parameter in the presence of GVL shows that the  
 250 addition of this solvent does not affect the swelling behavior of the catalyst.

251

252 3.2 Evaluation of external and internal mass transfer

253 -External mass transfer

254 Figs 4 show the effect of stirring rate on the kinetics of fructose alcoholysis. One can notice that the  
 255 fructose consumption is higher at 800 rpm than at 500 rpm or 1000 rpm (Fig. 4A). The fact that the  
 256 kinetics decreases from 1000 to 800 rpm is undoubtedly due to the vortex effect. Similar observation  
 257 can be done for BL, HMF and BMF concentration ratio (Fig. 4D, 4B, 4C). To decrease the effect of  
 258 external mass transfer resistance, experiments were performed at 800 rpm.

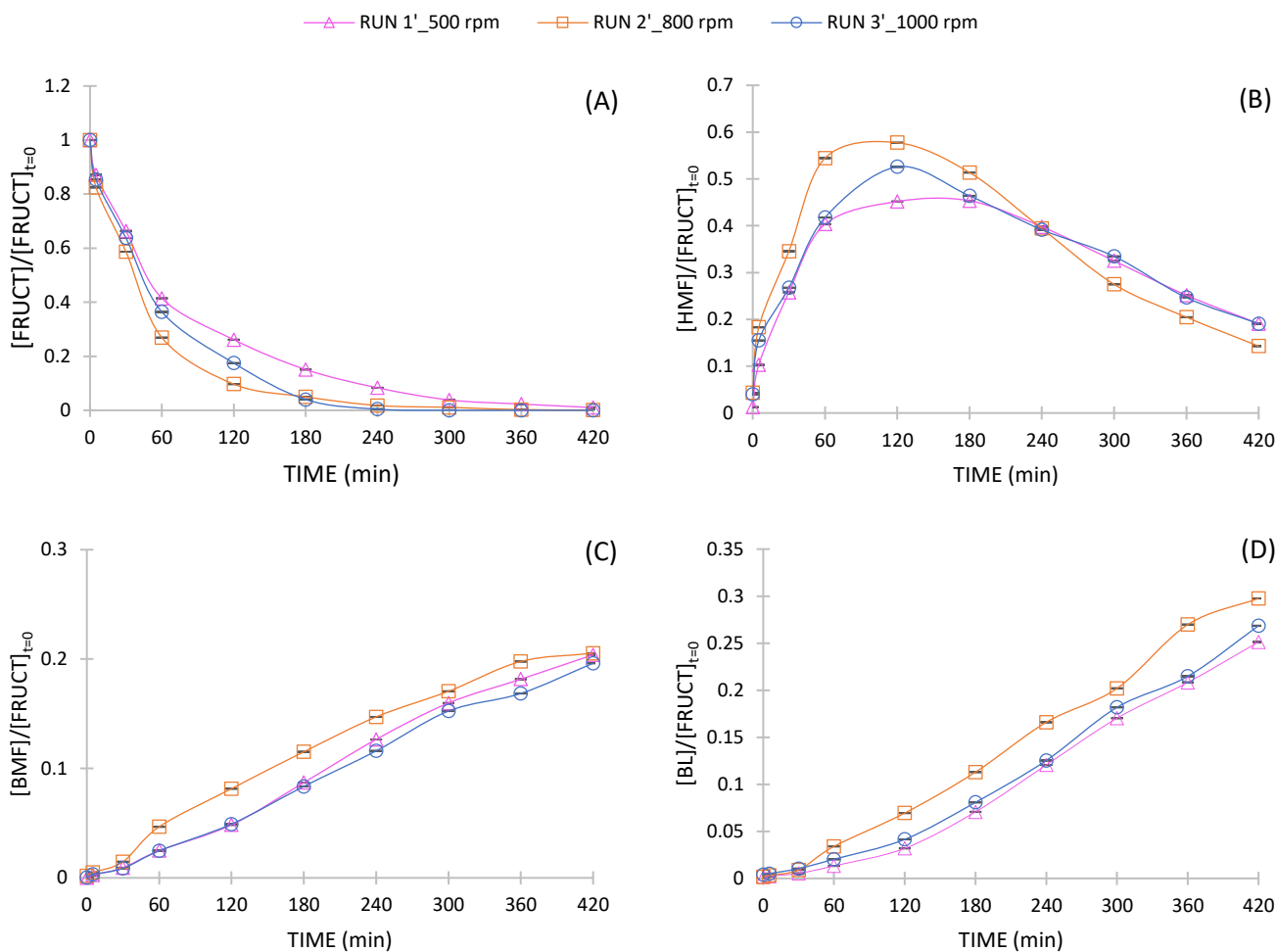


Fig. 4. Effect of the stirring rate on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

259

260

261

262 -Internal mass transfer

263 Figs 5 show the effect of catalyst PSD on the fructose alcoholysis. One can notice that in the operating  
264 conditions of this study, the catalyst PSD of Amberlite IR120 has a very negligible effect on the trends  
265 of fructose consumption (Fig. 5A), on HMF production (Fig. 5B), on BMF production (Fig. 5C), and on  
266 BL production (Fig. 5D). Thus, the internal mass transfer resistance can be considered to be negligible.

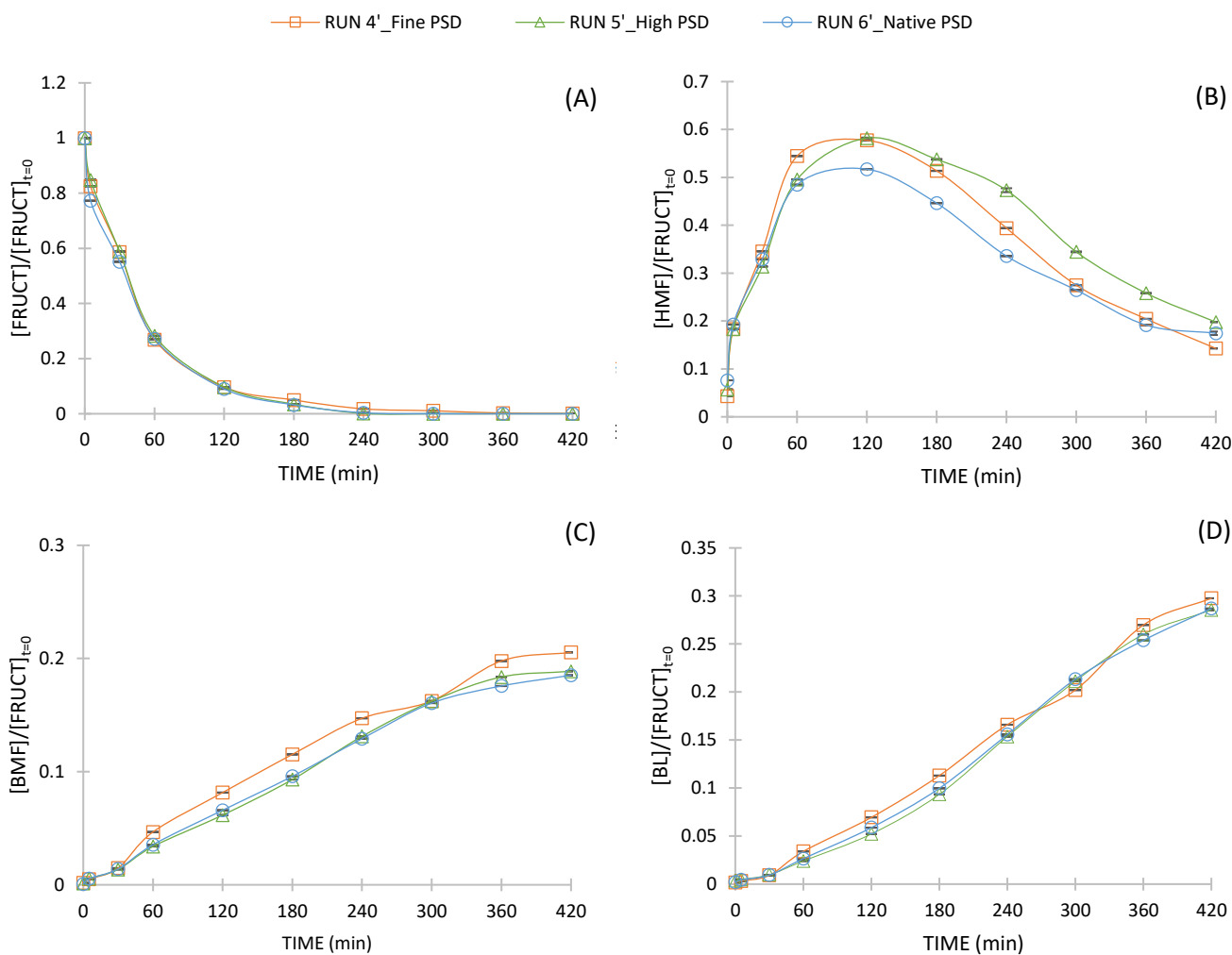


Fig. 5. Effect of catalyst PSD on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

267  
268 Based on external and internal mass transfer study, the experiments were performed with native PSD  
269 and at 800 rpm to avoid the interferences with mass transfer limitation.

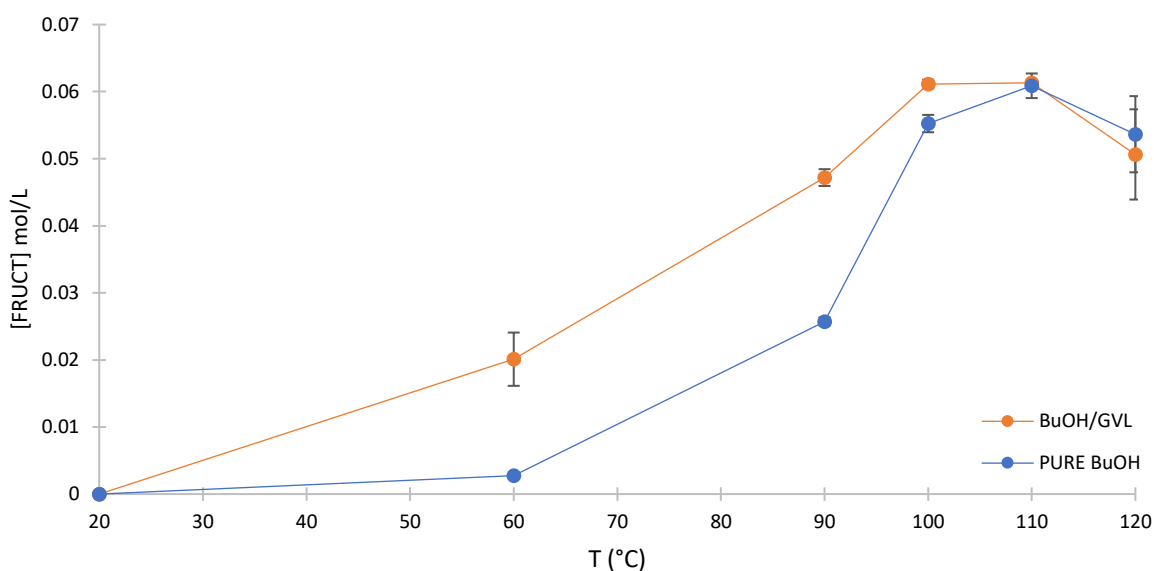
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272 3.3 Dissolution investigation

273 In the presence of water, even at low concentrations, it was observed that fructose dissolution could be  
274 considered instantaneously. For that reason, the dissolution of fructose in a 70/30 wt% BuOH/GVL and  
275 pure butanol solvent was studied.

276 The benefit of a 70/30 wt% BuOH/GVL compared to a pure butanol solution was found through fructose  
277 dissolution. Fig. 6 shows that fructose solubility increases with temperature up to 110°C, fructose  
278 degradation to humins is significant. Fructose dissolution results faster in a 70/30 wt% BuOH/GVL  
279 solvent for temperature lower than 100°C, already reaching 33% of total concentration at 60°C and  
280 complete dissolution at 100°C. The effect of BuOH/GVL solution in promoting fructose dissolution at  
281 temperatures below 100 °C could be advantageous for catalysts suffering from thermal instability.



282  
283 Fig. 6. Fructose dissolution in pure butanol and GVL/BuOH (30/70 wt%) solvents versus temperature.  
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292 3.4 Analysis of the effect of solvents in the alcoholysis of fructose.

293 - Butanol-Water

294 From Fig. 7A, it is not possible to observe a clear trend concerning the role of water concentration on  
295 the kinetics of fructose consumption since its reduction is due simultaneously to its rapid conversion to  
296 HMF and degradation to humins. The trends of HMF production and consumption give a better insight  
297 into the role of water. In Fig. 7B, HMF consumption is faster and total in the absence of water (Run 4,  
298 Fig. 7B), whereas at the highest water concentration, 17 wt% (i.e., Run 1, Fig. 7B), its conversion is  
299 slower. In high-water content, HMF is still present after 7 h, with a final yield of 18.3 %. The same water  
300 effects are also reflected in BMF concentration trends (Fig. 7C). BMF shows an upward concentration  
301 trend throughout the reaction time with 17 wt% of water (Run 1); by reducing the water concentration,  
302 the consumption phase of this intermediate becomes more and more pronounced. From Fig. 7C, the  
303 fastest kinetic is obtained in the absence of water, where the maximum of BMF is achieved at 180  
304 minutes. This observation is confirmed by Fig. 7D where the BL production is faster and higher by  
305 reducing the water content. The increase in BL production, i.e., in yield of BL, by decreasing the water  
306 content is also directly related to the moles of fructose lost during the reaction time. Table 6 reports the  
307 fructose loss (mol%) due to by-sides reactions, as degradation to humins, which amounts to around  
308 22% with 17% water and is reduced to 1.5% in the absence of water, increasing BL yield of up to 57.5%.  
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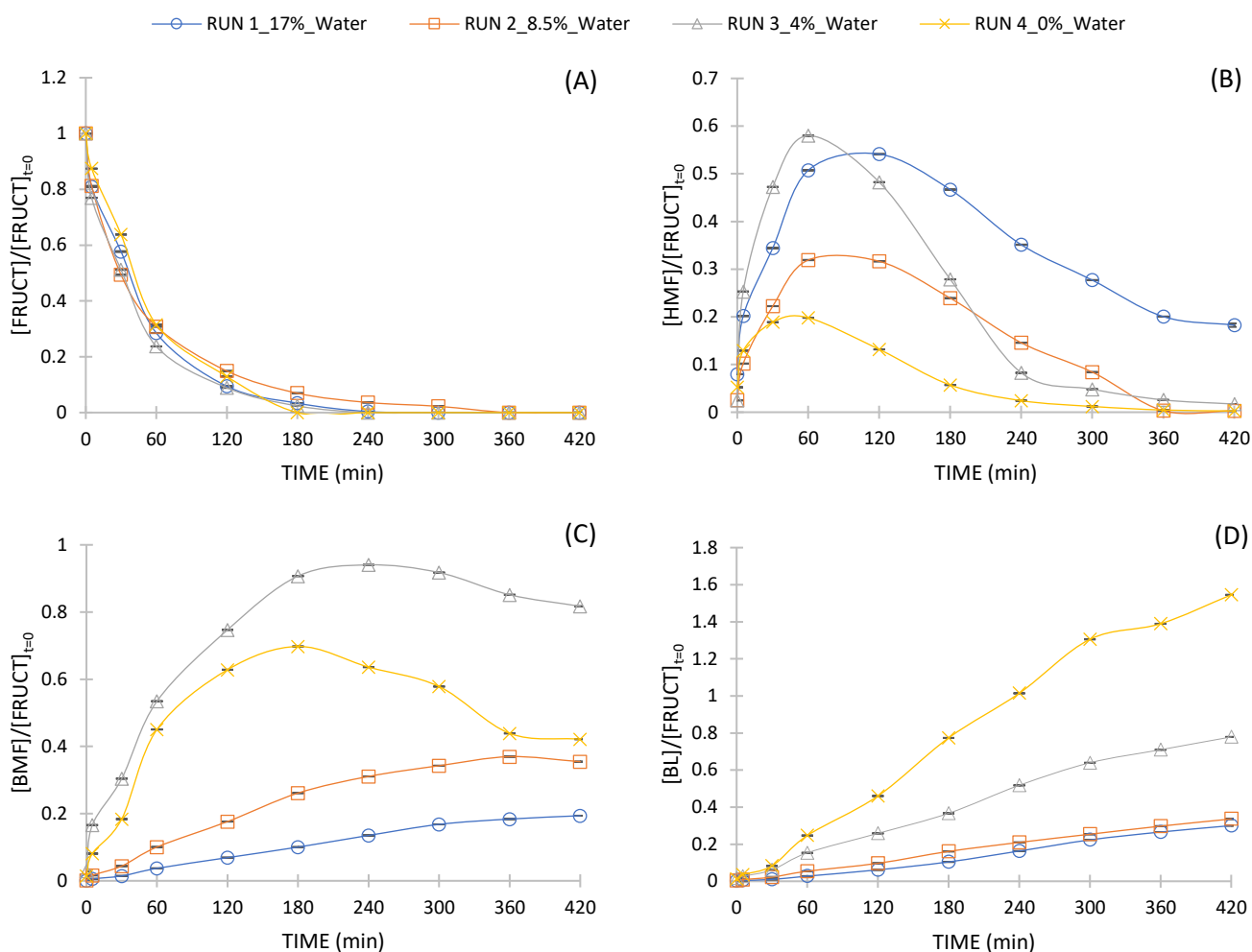


Fig. 7. Effect of water concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL

311

312 These results may confirm the role of water in affecting the stability of fructose in alcoholic medium,  
 313 favoring its degradation to humins by-product [44,46,48]. Besides, to increase fructose loss into humins,  
 314 the role of the water in inhibiting catalytic action of ion exchange resins, as suggested by some research  
 315 [70,71].

316

317 Table 6: Fructose moles lost in butanol-water solvent (110 °C, fructose initial conc. 11 g/L, catalyst  
 318 loading 35 g/L).

Run	Butanol (wt%)	Water (wt%)	GVL (wt%)	Fructose lost mol%
1	83	17	0	22.2
2	91.5	8.5	0	16.1
3	96	4	0	5.7
4	100	0	0	1.5

319

320

321 - Butanol-Water (8.5wt%)-GVL

322 In these experiments, the effect of aprotic polar solvent, namely GVL, was evaluated in the solvent polar  
323 protic mixture butanol-water. In this system, 8.5 wt% water was added as the minimum water content to  
324 achieve the fastest fructose dissolution and thus neglect the dissolution effect on reaction kinetics.

325 Fig. 8A shows that the kinetics of fructose consumption is faster at the highest GVL concentration (i.e.,  
326 Run 5). When the concentration of GVL is lower, the kinetics of fructose consumption is slower (Fig.  
327 8A). This could derive from the ability of GVL to promote further the dissolution of fructose in the alcohol  
328 medium, as demonstrated in the dissolution study, by facilitating the interaction with the catalyst.

329 However, the rapid fructose conversion in GVL excess is not reflected in the HMF production and  
330 consumption trend, which is faster when GVL concentration decreases (Fig. 8B). This may be because

331 the reaction pathway seems to change in excess of GVL. In contrast to the other experiments, a modest  
332 concentration of LA was produced in Run 5, with yields in LA of up to 15%. LA was not identified in Runs  
333 5 and 6, where high concentrations of the intermediate BMF can be found. HMF concentration trends in

334 30 wt% (Run 5) and 15 wt% (Run 6) are similar, with a higher HMF concentration produced in the case  
335 of 30 wt% of GVL. In both solvent systems, a residual HMF concentration can be found after 7 hours, in  
336 contrast to Run 2 where a complete conversion of HMF is observed for the same water content. This

337 may highlight the role of the aprotic solvent in stabilizing reaction intermediates such as HMF. The same  
338 trend was also observed for the BMF consumption and production concentration trends (Fig. 8C). From

339 Fig. 8C, the production of BMF is remarkably low at the highest GVL concentration, as a result of LA  
340 production by HMF rehydration, and with an optimal production trend in 30 wt% GVL. Fig. 8D shows

341 that high GVL concentration does not increase the BL production in the reaction time considered,  
342 possibly due to slower LA esterification kinetics to BL than BMF conversion and a non-excess of alcohol

343 in the medium. GVL concentration between 15 and 30 wt% gives a higher BL concentration. Low GVL  
344 amount improves the production of BL compared to Run 2 in terms of yields, but a higher GVL amount

345 is detrimental for BL production (Fig. 8D). The beneficial role of GVL is also demonstrated by evaluating  
346 the secondary consumption of fructose moles (Table 7), where the addition of GVL can result in up to

347 5% less of fructose lost, compared to the solvent butanol-water. As an optimum in terms of BL production  
348 and fructose mole loss, experimental results indicate the addition of 30 wt% GVL in the solvent medium.

349

350 Table 7: Fructose moles lost in butanol-water-GVL solvent, compared with Run 2 (110 °C, fructose  
351 initial conc. 11 g/L, catalyst loading 35 g/L).

Run	Butanol (wt%)	Water (wt%)	GVL (wt%)	Fructose lost mol%
2	91.5	8.5	0	16.1
5	2.5	8.5	89	9.1
6	60.5	8.5	30	10
7	76.5	8.5	15	11.9

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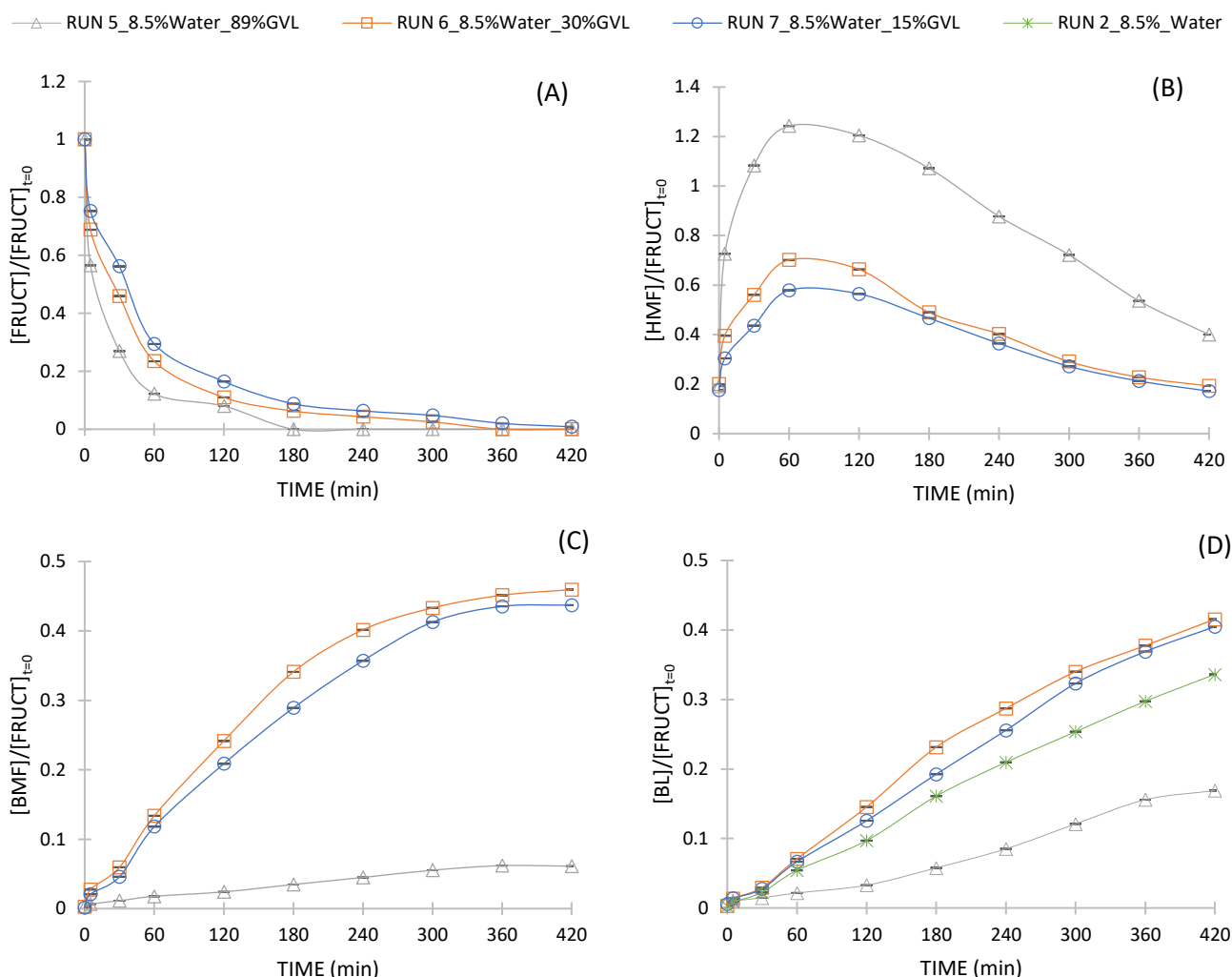


Fig. 8. Effect of GVL concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

358

359 - Butanol-GVL in the absence of water

360 Previous results showed that water does not improve the fructose alcoholysis to butyl levulinate. From  
 361 Run 6, the addition of 30 w% of GVL increases the BL yield. A further investigation was done by  
 362 performing an experiment with 30 w% of GVL in the absence of water (Run 8). Fig. 9A shows that  
 363 fructose consumption in a 30 wt% GVL (Run 8) is slower than pure butanol. This result may be due to  
 364 GVL ability to limit unwanted degradation reaction to humins, resulting in higher selectivity to reaction  
 365 intermediates such as HMF and BMF. In fact, the production of HMF and BMF is more important at 30  
 366 wt% of GVL (Figs 9B and C). In 30 wt% GVL, HMF is still present in moderate concentration after 7  
 367 hours, whereas in pure butanol, it rapidly reaches complete conversion. As with fructose, this could be  
 368 due to the role of GVL in stabilising the HMF intermediate and limiting its degradation. This is also

369 reflected in the reduction of the moles of fructose lost, which are approximately zero in the presence of  
 370 GVL and greater than 1% in pure alcohol, as shown in Table 8. This observation is confirmed by Fig.  
 371 9D where the concentration of BL increases at 30 wt.% of BL. Although the consumption kinetics of  
 372 fructose and intermediates are slower in the presence of GVL, the production of BL is higher and faster  
 373 than in pure butanol.

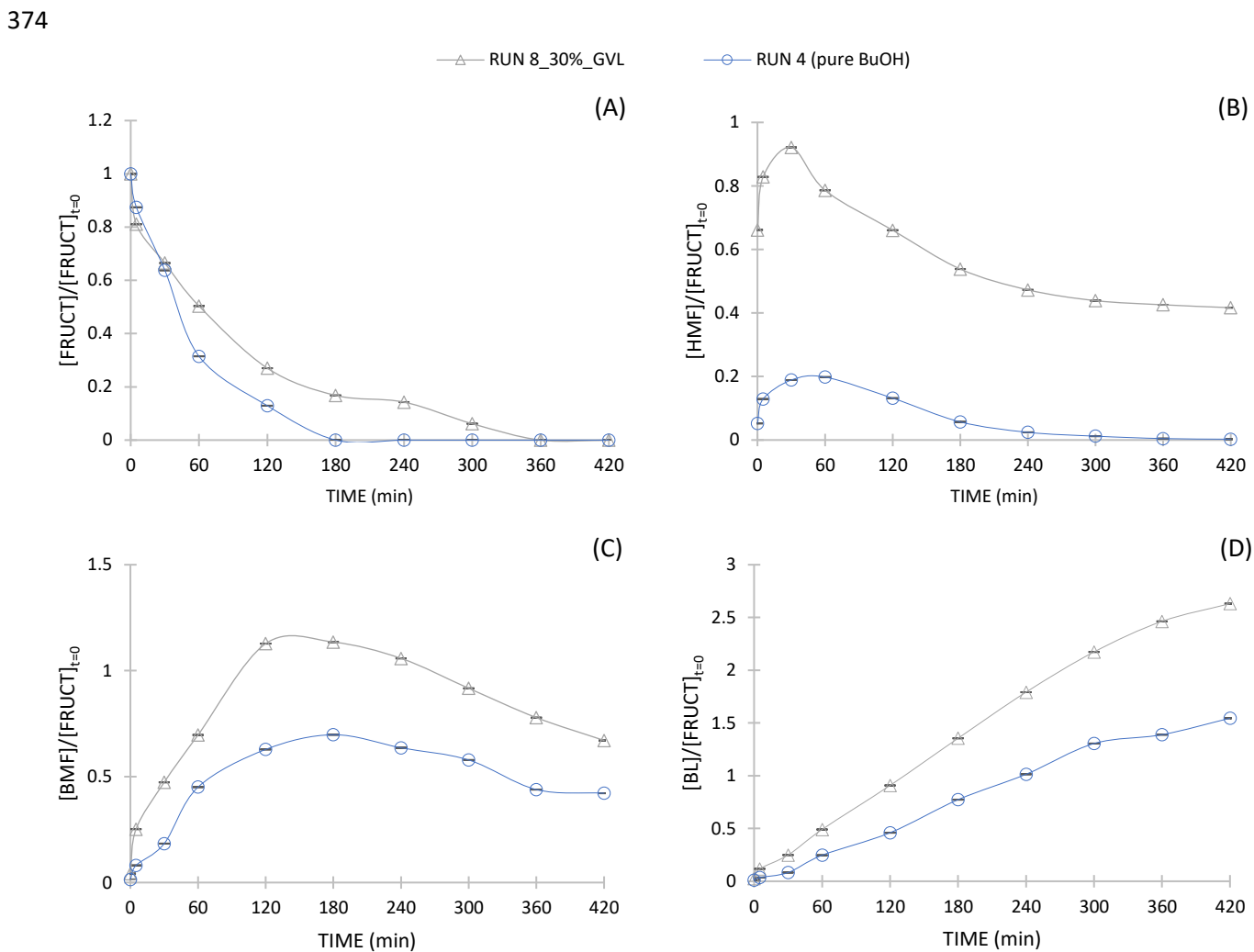


Fig. 9. Effect of BuOH/GVL concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

375  
 376 Table 8: Comparison fructose moles lost in run 4 and 8 (110 °C, fructose initial conc. 11 g/L, catalyst  
 377 loading 35 g/L).

Run	Butanol wt%	Water wt%	GVL wt%	Fructose lost mol%
4	100	0	0	1.5
8	70	0	30	0

### 379 3.5 Comparison with literature data

380 Table 9 compared the literature data of fructose solvolysis to BL over different solid acid catalysts with  
381 the most promising obtained in this study. Since other reaction conditions are used, the comparison is  
382 not directly straightforward. Considering the same cross-linking grade (DVB%=8), since it directly affects  
383 the catalytic activity [43], Amberlite IR120 has been compared with Amberlyst 39 and Dowex 50Wx8. In  
384 the presence of water, the yield of BL obtained with Amberlite IR120 (entry 3) is slightly higher than the  
385 corresponding with Dowex50Wx8 (entry 5) and Amberlyst 39 (entry 6), considering a higher catalyst  
386 loading but a lower temperature and a lower acid capacity (4.4 m<sub>eq</sub>/g versus 4.83 m<sub>eq</sub>/g of Dowex 50Wx8  
387 and 4.82 m<sub>eq</sub>/g of Amberlyst 39, respectively [43]). The elimination of water from the solvent mixture  
388 drastically affects the production of BL, increasing the yield to 57.5 % (entry 2) in pure butanol, from  
389 30.0 % (entry 3) in the presence of 17 wt% of water. This is due to the role of water in the degradative  
390 consumption of fructose leading to up to 22% of fructose moles lost, and secondly, its possible inhibiting  
391 effect on the catalytic activity of the resin. As shown, the BL yield increased significantly, reaching values  
392 comparable to those in the literature for other solid acid catalysts. An et al. [33] reported a 62.8 % of BL  
393 yield in the presence of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> at 190 °C; Kuo et al. [72] obtained 67 % of BL yield by using TiO<sub>2</sub>  
394 nanoparticles at 150 °C; Balakrishnan et al. [73] found lower yields by using Dowex 50Wx8 resin, maybe  
395 due to the high catalyst loading.

396 Table 9 shows that the BL production is further improved by introducing GVL in butanol solvent system  
397 (30/70 wt%), leading to 60.4 % yield (entry 1). The presence of GVL also led to an increase in HMF and  
398 BMF selectivity, resulting in a higher residual concentration of these intermediates after the reaction  
399 time compared to the case of pure butanol. The addition of GVL determined a strong reduction in  
400 fructose moles lost, up to 7% less in a solvent system with water (Table 7, run 2 versus 6), and no moles  
401 lost in BuOH/GVL solvent system (table 8, run 8). The effect on fructose moles balance and the residual  
402 intermediate concentrations may suggest that GVL prevents the consumption of fructose and HMF by  
403 secondary reactions, such as degradation to humins, and that even higher BL yields could be expected  
404 by increasing the contact time.

405 In summary, fructose alcoholysis on Amberlite IR120 achieved good BL yields, comparable to those  
406 obtained in other studies but significant in energy savings under more moderate temperature conditions.  
407 The use of GVL in the alcohol medium increased the butyl levulinate production and resulted in faster  
408 dissolution of fructose, promising benefits from the perspective of considering production from higher  
409 concentrations of fructose.

410

Table 9: Comparison with literature data on fructose alcoholysis to butyl levulinate.

Entry	Catalyst	T (°C)	t (h)	Fructose (g/L)	Solvent (wt%)	$\omega_{\text{CAT}}$ (g/L)	$X_{\text{fruct}}$ %	$Y_{\text{BL}}$ %	Ref.	
1	Amberlite IR120	110	7	11	BuOH/GVL	70/30	35	100	<b>60.4</b>	This study
2		110	7	11	BuOH	-	35	100	<b>57.5</b>	
3		110	7	11	BuOH/Water	83/17	35	100	<b>30.0</b>	
4	Dowex 50Wx8	110	30	72	BuOH	-	260	97	<b>14.0</b>	[73]
5		120	6	21	BuOH/Water	83/17	14.3	>99.5	<b>24.2</b>	[43]
6	Amberlyst 39	120	6	21	BuOH/Water	83/17	14.3	>99.5	<b>25.3</b>	
7	$\text{Fe}_2(\text{SO}_4)_3$	190	3	25	BuOH	-	5	>99	<b>62.8</b>	[33]
8	$\text{TiO}_2$	150	1	20	BuOH	-	5	100	<b>67.0</b>	[72]
9	CNT-PSSA	120	12	12.5	BuOH	-	5	99	<b>78.0</b>	[29]

411

412



413 **4. Conclusions**

414 The alcoholysis of biomass-derived fructose into promising fuel additive n-butyl levulinate over ion  
415 exchange resins was studied in this research, showing the benefits of polar aprotic solvent GVL in terms  
416 of fructose dissolution and production of BL.

417 The swelling behavior of the catalyst was studied and found to be independent of the nature of the  
418 solvents tested. Furthermore, it has been shown that the influence of external and internal mass transfer  
419 can be neglected using 800 rpm of rotating speed and the native particle size distribution by using our  
420 experimental setup.

421 Among the solvent mixtures tested, BuOH/GVL (70/30 wt%) has increased fructose dissolution  
422 compared to pure butanol. Fructose dissolution was faster in BuOH/GVL (70/30 wt%) between 20 and  
423 100°C, achieving complete dissolution at 100 °C. Temperature higher than 110 °C results in significant  
424 degradation of fructose in both solvents.

425 The influence of water and GVL co-solvent (polar aprotic) were investigated on the kinetics of fructose,  
426 HMF, BMF and BL. The addition of water did not improve BL production kinetics, although it promotes  
427 the rapid dissolution of fructose even at low temperatures. At the contrary, BL yield increased from 30  
428 % with 17 wt% of water to 57.5 % in the absence of water. Finally, the yield was further increased to  
429 60.4 % by adding 30 wt% of GVL in butanol.

430 Considering the fructose dissolution and kinetic results, the use of BuOH/GVL (70/30 wt%) solvent is  
431 the best solution in the alcoholysis of fructose to butyl levulinate over solid acid catalyst.

432

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