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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].

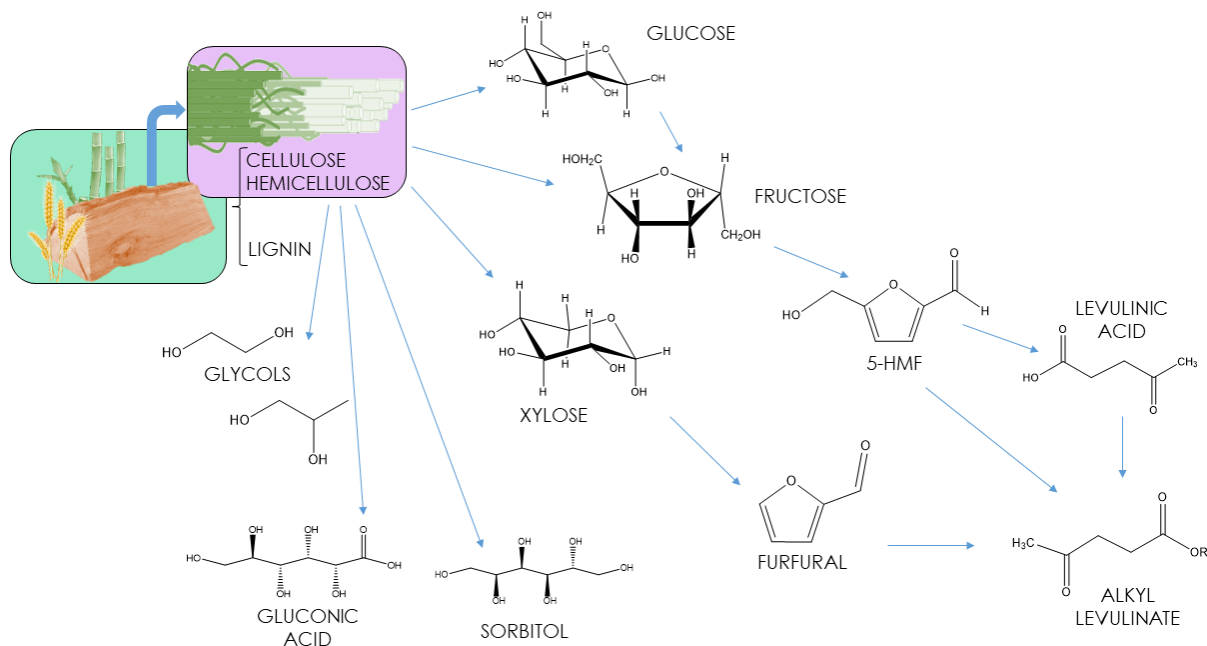


Fig. 1. Valorization of cellulose adapted from literature [18].

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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_x 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, γ -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 γ -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-NH₂ column (250 mm x
132 4.6 mm x 5 μ 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 μ m x 0.25
136 μ 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 (ω_{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% | ω_{CAT} (g/L) | T(°C) | rpm | Reaction time (h) | Inert gas |
|---------------|-----|--------------|-------------|-----------|---------|-----------------------------|-------|-----|-------------------|-------------------------|
| No GVL | 1 | 1.6 | 83 | 17 | 0 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 2 | 1.6 | 91.5 | 8.5 | 0 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 3 | 1.6 | 96 | 4 | 0 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 4 | 1.6 | 100 | 0 | 0 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| GVL | 5 | 1.6 | 2.5 | 8.5 | 89 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 6 | 1.6 | 60.5 | 8.5 | 30 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 7 | 1.6 | 76.5 | 8.5 | 15 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 8 | 1.6 | 70 | 0 | 30 | 35 | 110 | 800 | 7 | N ₂ (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 (μm) | $\geq 94 \%$ ($300 < d < 1180 \mu m$) |

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 μm and the remaining particles with diameters between 300 and 500 μm . 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% | ω_{CAT} (g/L) | T($^{\circ}C$) | rpm | t(h) | Inert gas |
|-------------|-----|--------|-----------------|----------------|--------------|-------------------------|------------------|------|------|-------------------------|
| Ext. | 1' | Fine | 1.6 | 83 | 17 | 35 | 110 | 500 | 7 | N ₂ (20 bar) |
| | 2' | Fine | 1.6 | 83 | 17 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 3' | Fine | 1.6 | 83 | 17 | 35 | 110 | 1000 | 7 | N ₂ (20 bar) |
| Int. | 4' | Fine | 1.6 | 83 | 17 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 5' | High | 1.6 | 83 | 17 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |
| | 6' | Native | 1.6 | 83 | 17 | 35 | 110 | 800 | 7 | N ₂ (20 bar) |

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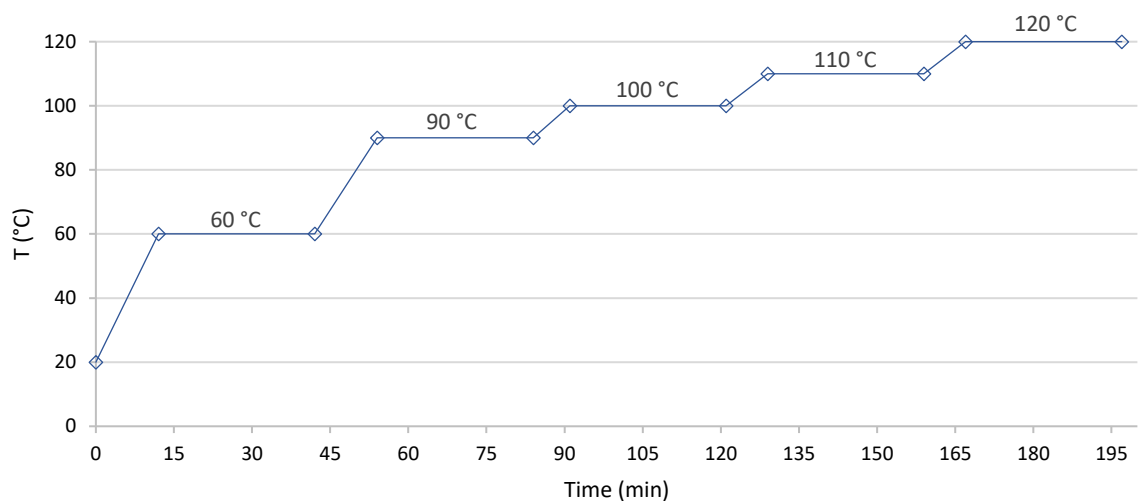
189 Being characterized by cross-linked styrene-divinylbenzene, the particle size of Amberlite IR120 is also
190 affected by the swelling effect due to the solvent. In other words, even if the amount of dried catalyst is
191 the same, the kinetics could be different if the solvent is different due to 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).



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

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Table 4: Experimental matrix for fructose dissolution study.

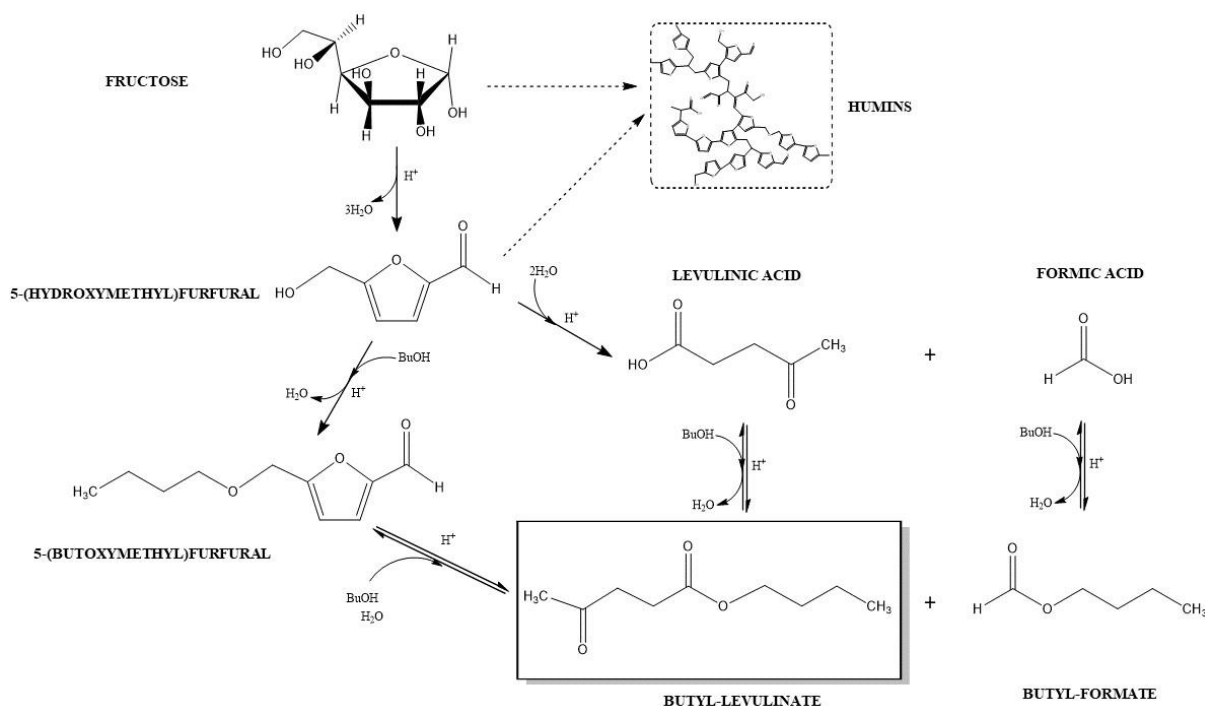
| RUN | Fructose (g) | Butanol wt% | GVL wt% | rpm | Inert gas |
|-----|--------------|-------------|---------|-----|-------------------------|
| S1 | 1.6 | 100 | 0 | 800 | N ₂ (20 bar) |
| S2 | 1.6 | 70 | 30 | 800 | N ₂ (20 bar) |

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].



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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.

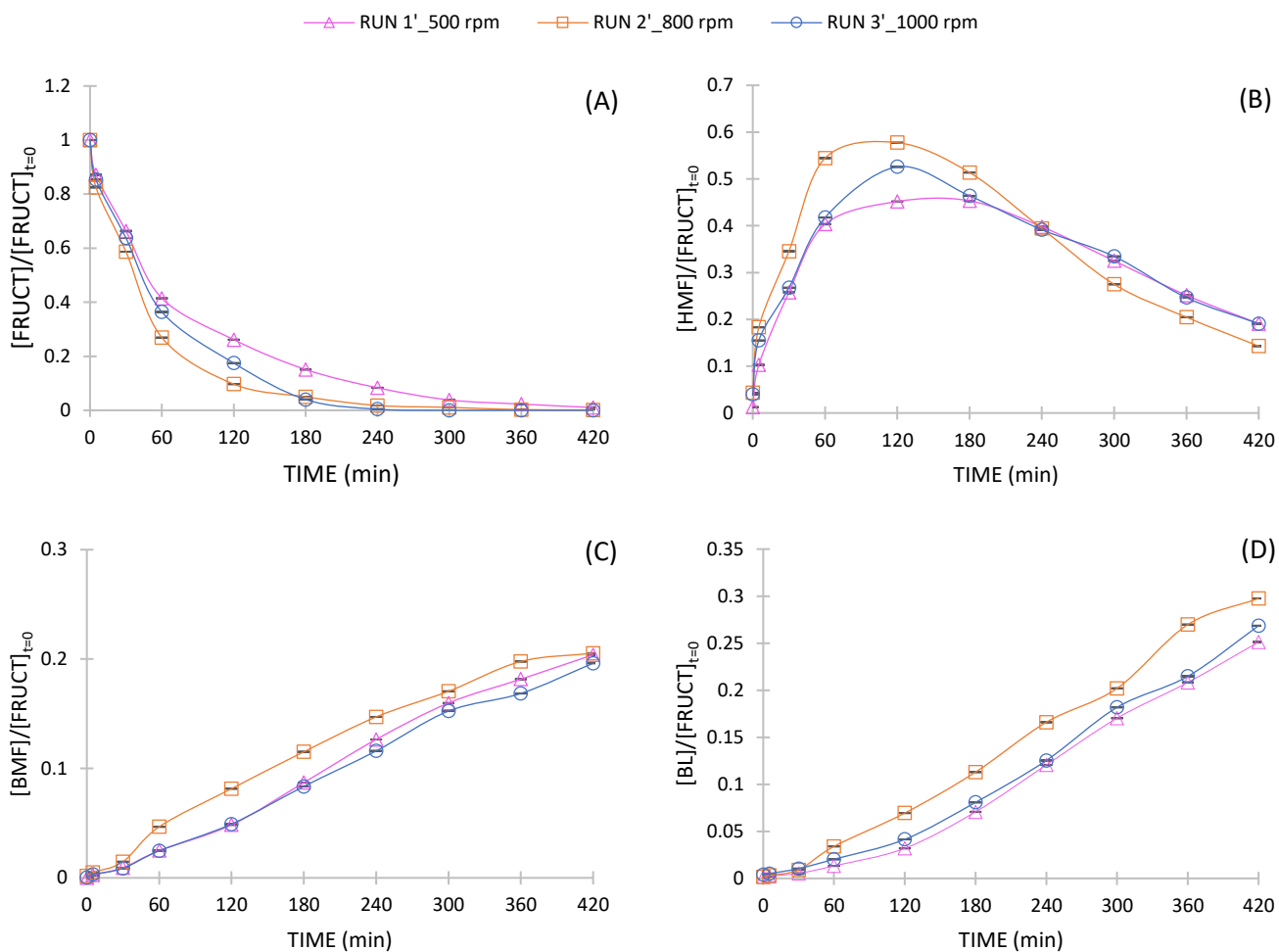


Fig. 4. Effect of the stirring rate on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

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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.

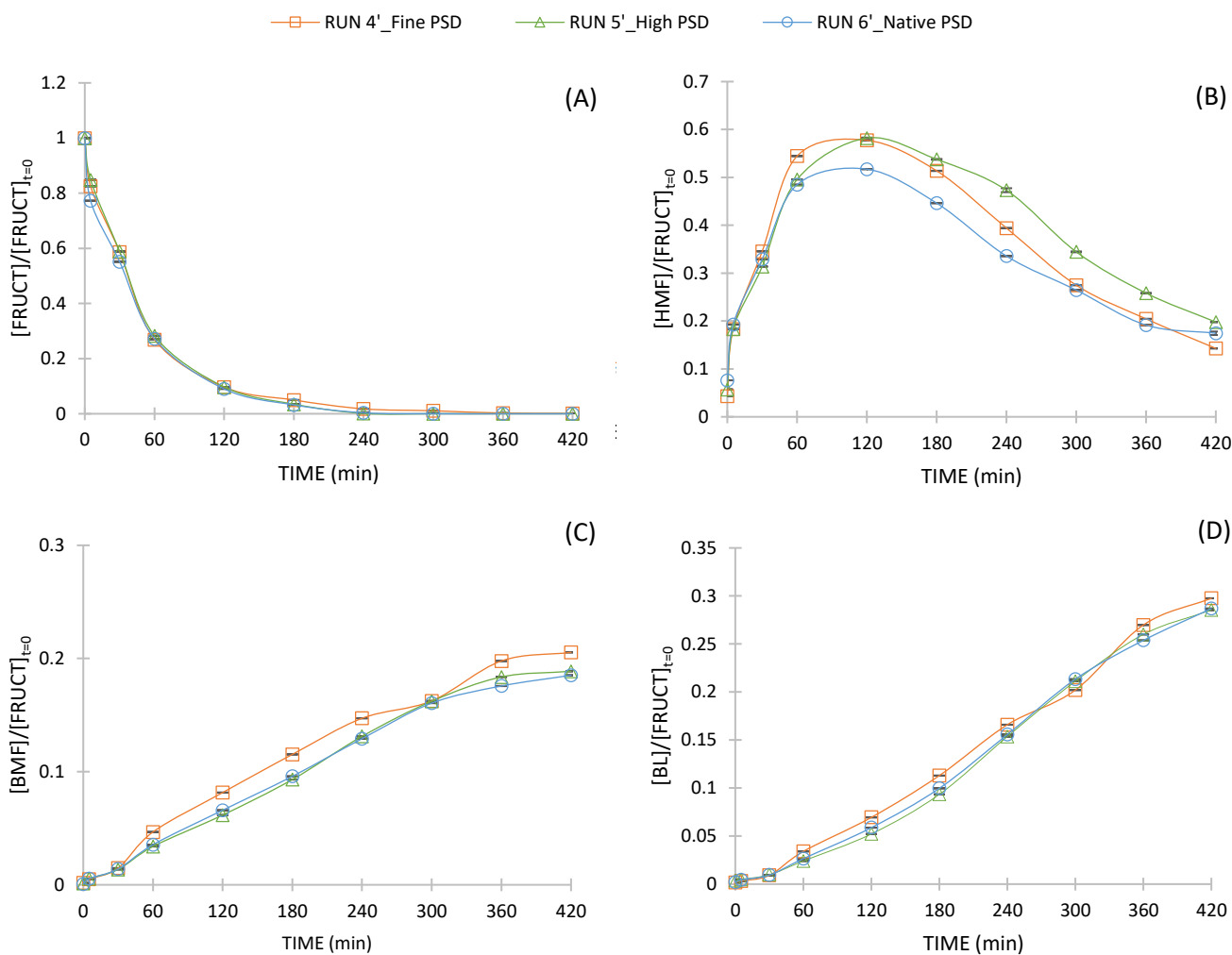


Fig. 5. Effect of catalyst PSD on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

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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.

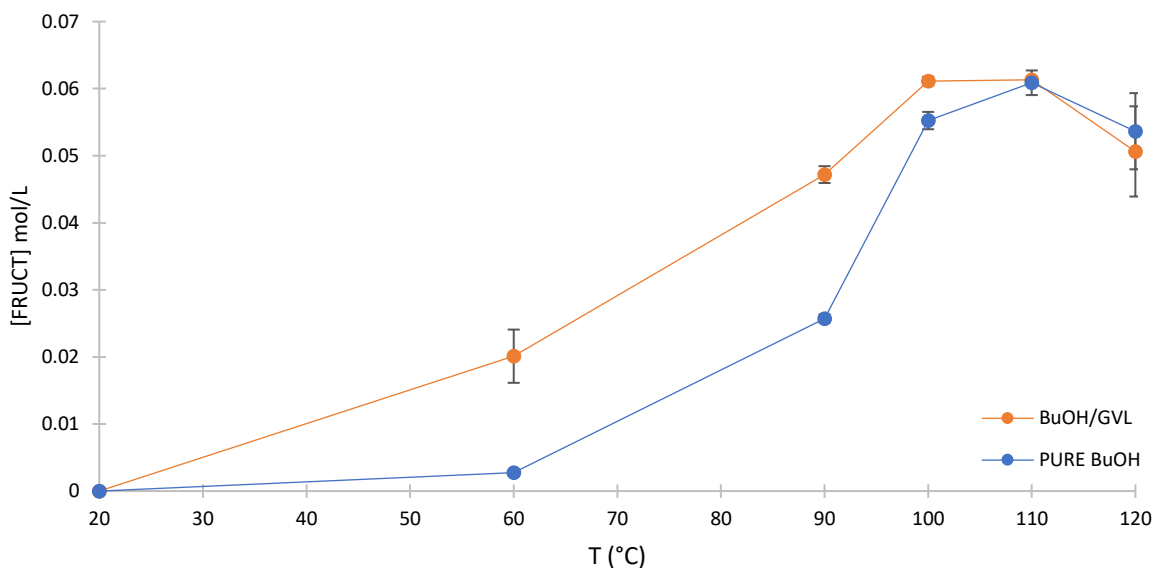
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272 3.3 Dissolution investigation

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%.
309
310

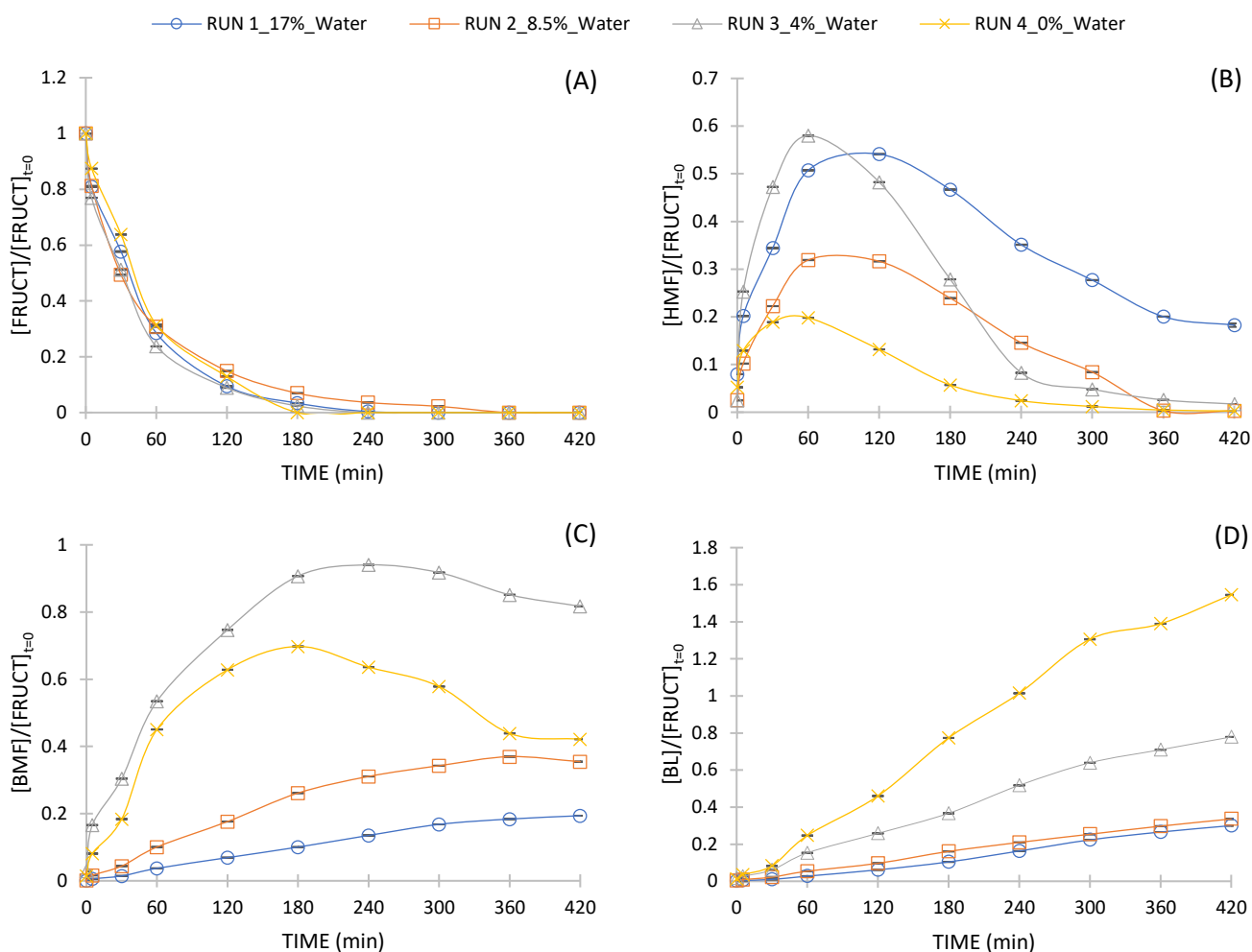


Fig. 7. Effect of water concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL

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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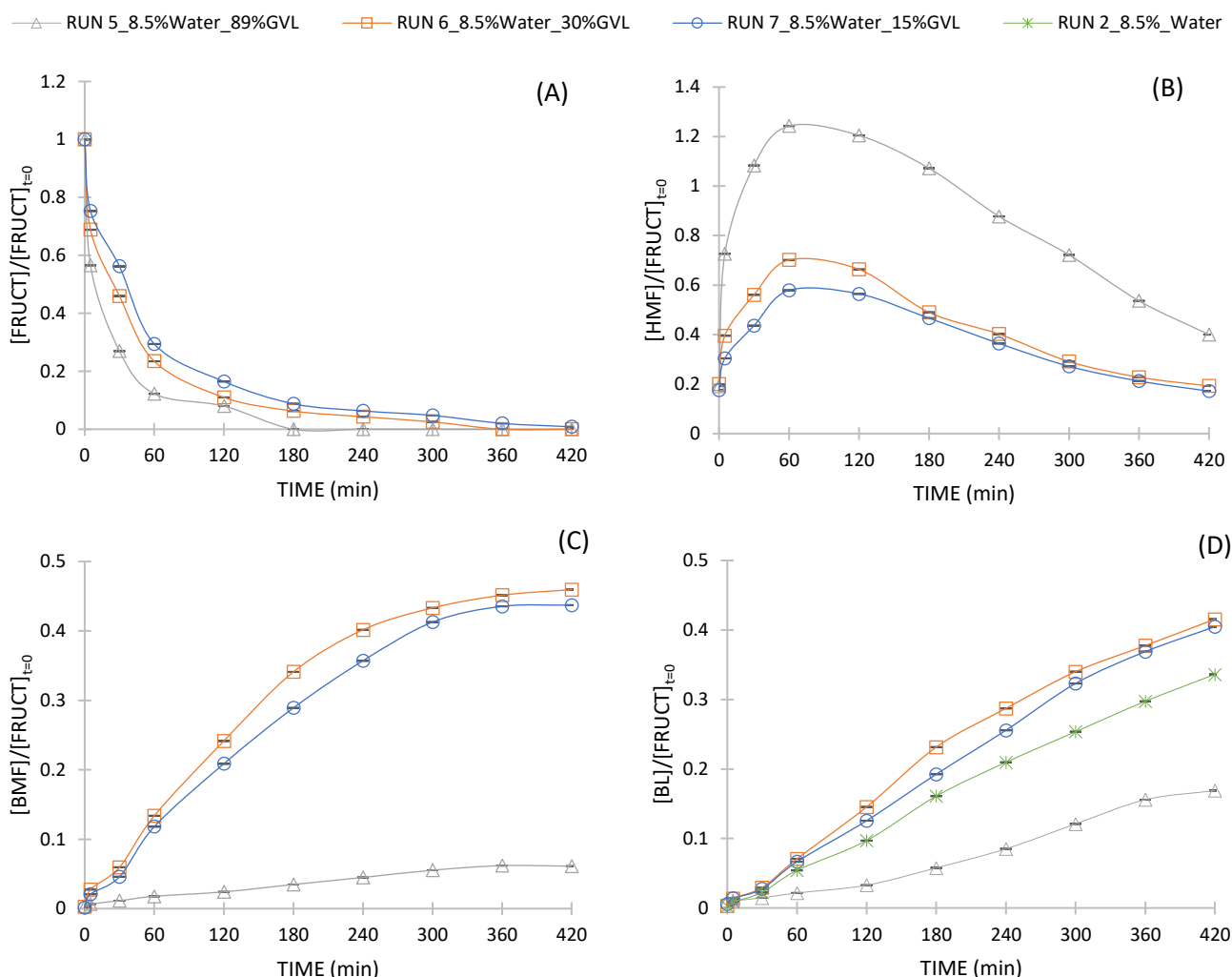


Fig. 8. Effect of GVL concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

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.

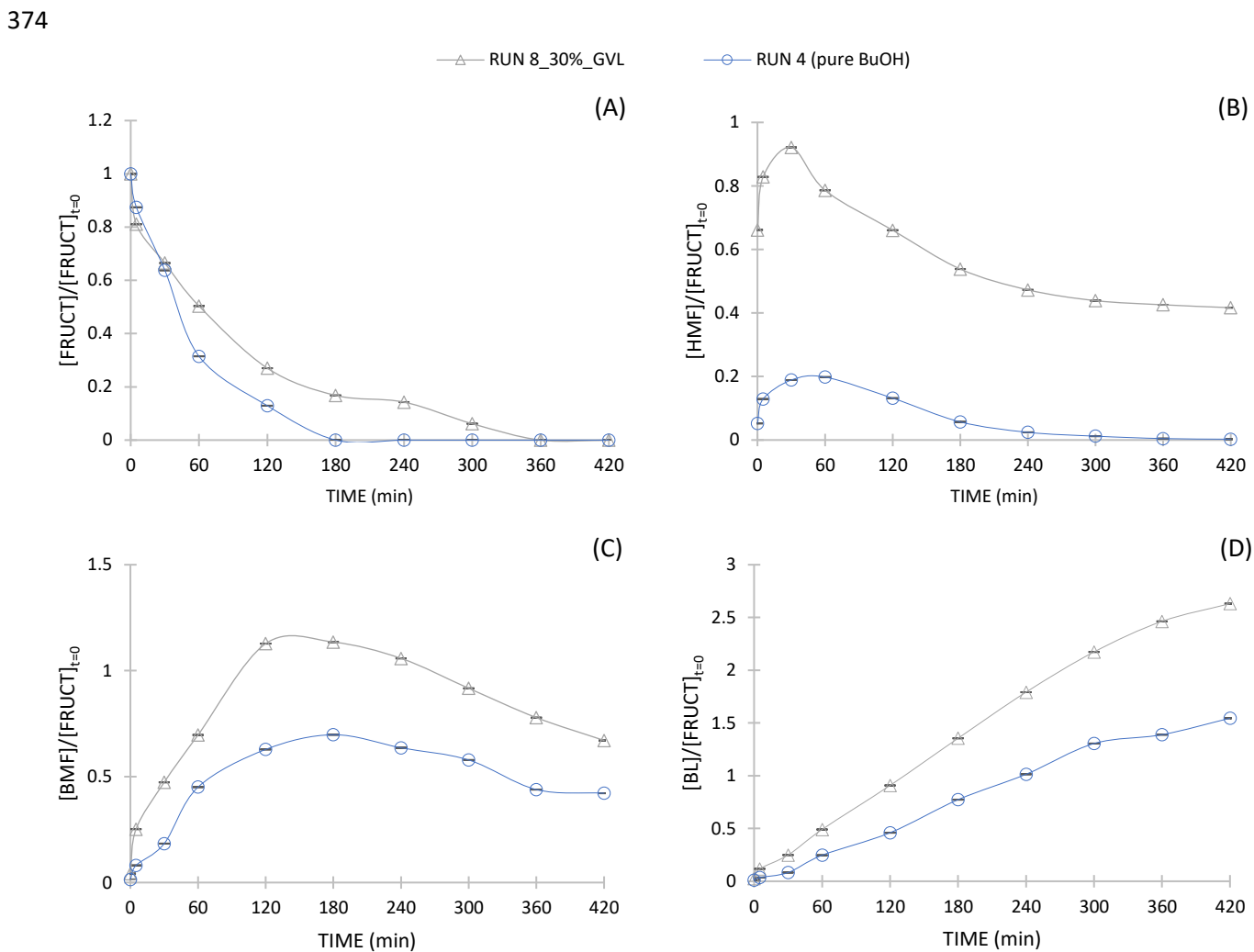


Fig. 9. Effect of BuOH/GVL concentration on the concentrations (normalised with respect to the fructose concentration at time zero): (A) fructose, (B) HMF, (C) BMF, and (D) BL.

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 meq/g versus 4.83 meq/g of Dowex 50Wx8
387 and 4.82 meq/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 $\text{Fe}_2(\text{SO}_4)_3$ at 190 °C; Kuo et al. [72] obtained 67 % of BL yield by using TiO_2
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%) | ω_{CAT} (g/L) | X_{fruct} % | Y_{BL} % | Ref. | |
|-------|------------------------------|--------|-------|----------------|---------------|-----------------------------|----------------------|-------------------|-------------|------------|
| 1 | Amberlite IR120 | 110 | 7 | 11 | BuOH/GVL | 70/30 | 35 | 100 | 60.4 | This study |
| 2 | | 110 | 7 | 11 | BuOH | - | 35 | 100 | 57.5 | |
| 3 | | 110 | 7 | 11 | BuOH/Water | 83/17 | 35 | 100 | 30.0 | |
| 4 | Dowex 50Wx8 | 110 | 30 | 72 | BuOH | - | 260 | 97 | 14.0 | [73] |
| 5 | | 120 | 6 | 21 | BuOH/Water | 83/17 | 14.3 | >99.5 | 24.2 | [43] |
| 6 | Amberlyst 39 | 120 | 6 | 21 | BuOH/Water | 83/17 | 14.3 | >99.5 | 25.3 | |
| 7 | $\text{Fe}_2(\text{SO}_4)_3$ | 190 | 3 | 25 | BuOH | - | 5 | >99 | 62.8 | [33] |
| 8 | TiO_2 | 150 | 1 | 20 | BuOH | - | 5 | 100 | 67.0 | [72] |
| 9 | CNT-PSSA | 120 | 12 | 12.5 | BuOH | - | 5 | 99 | 78.0 | [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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446

447 **References**

- 448 [1] Valentine J, Clifton-Brown J, Hastings A, Robson P, Allison G, Smith P. Food vs. fuel: the use of
449 land for lignocellulosic 'next generation' energy crops that minimize competition with primary food
450 production. *Global Change Biol Bioenergy* 2012;4:1–19. [https://doi.org/10.1111/j.1757-](https://doi.org/10.1111/j.1757-1707.2011.01111.x)
451 [1707.2011.01111.x](https://doi.org/10.1111/j.1757-1707.2011.01111.x).
- 452 [2] Wagle A, Angove MJ, Mahara A, Wagle A, Mainali B, Martins M, et al. Multi-stage pretreatment
453 of lignocellulosic biomass for multi-product biorefinery: A review. *Sustainable Energy Technologies and*
454 *Assessments* 2022;49:101702. <https://doi.org/10.1016/j.seta.2021.101702>.
- 455 [3] Oriez V, Peydecastaing J, Pontalier P-Y. Lignocellulosic Biomass Fractionation by Mineral Acids
456 and Resulting Extract Purification Processes: Conditions, Yields, and Purities. *Molecules* 2019;24:4273.
457 <https://doi.org/10.3390/molecules24234273>.
- 458 [4] Li M-F, Yang S, Sun R-C. Recent advances in alcohol and organic acid fractionation of
459 lignocellulosic biomass. *Bioresource Technology* 2016;200:971–80.
460 <https://doi.org/10.1016/j.biortech.2015.10.004>.
- 461 [5] Lu X, Lagerquist L, Eränen K, Hemming J, Eklund P, Estel L, et al. Reductive Catalytic
462 Depolymerization of Semi-industrial Wood-Based Lignin. *Ind Eng Chem Res* 2021;60:16827–38.
463 <https://doi.org/10.1021/acs.iecr.1c03154>.
- 464 [6] Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, et al. Lignin Valorization:
465 Improving Lignin Processing in the Biorefinery. *Science* 2014;344:1246843.
466 <https://doi.org/10.1126/science.1246843>.
- 467 [7] Rinaldi R, Jastrzebski R, Clough MT, Ralph J, Kennema M, Bruijninx PCA, et al. Paving the Way
468 for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew Chem Int*
469 *Ed* 2016;55:8164–215. <https://doi.org/10.1002/anie.201510351>.
- 470 [8] Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K. Bright Side of Lignin Depolymerization:
471 Toward New Platform Chemicals. *Chem Rev* 2018;118:614–78.
472 <https://doi.org/10.1021/acs.chemrev.7b00588>.

- 473 [9] Azadi P, Inderwildi OR, Farnood R, King DA. Liquid fuels, hydrogen and chemicals from lignin:
474 A critical review. *Renewable and Sustainable Energy Reviews* 2013;21:506–23.
475 <https://doi.org/10.1016/j.rser.2012.12.022>.
- 476 [10] Liu C, Wu S, Zhang H, Xiao R. Catalytic oxidation of lignin to valuable biomass-based platform
477 chemicals: A review. *Fuel Processing Technology* 2019;191:181–201.
478 <https://doi.org/10.1016/j.fuproc.2019.04.007>.
- 479 [11] Zhou M, Sharma BK, Li J, Zhao J, Xu J, Jiang J. Catalytic valorization of lignin to liquid fuels over
480 solid acid catalyst assisted by microwave heating. *Fuel* 2019;239:239–44.
481 <https://doi.org/10.1016/j.fuel.2018.10.144>.
- 482 [12] Kumar AK, Sharma S. Recent updates on different methods of pretreatment of lignocellulosic
483 feedstocks: a review. *Bioresour Bioprocess* 2017;4:7. <https://doi.org/10.1186/s40643-017-0137-9>.
- 484 [13] Zhang Z, Song J, Han B. Catalytic Transformation of Lignocellulose into Chemicals and Fuel
485 Products in Ionic Liquids. *Chem Rev* 2017;117:6834–80.
486 <https://doi.org/10.1021/acs.chemrev.6b00457>.
- 487 [14] Loow Y-L, Wu TY, Md. Jahim J, Mohammad AW, Teoh WH. Typical conversion of lignocellulosic
488 biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment. *Cellulose*
489 2016;23:1491–520. <https://doi.org/10.1007/s10570-016-0936-8>.
- 490 [15] Luo Y, Li Z, Li X, Liu X, Fan J, Clark JH, et al. The production of furfural directly from hemicellulose
491 in lignocellulosic biomass: A review. *Catalysis Today* 2019;319:14–24.
492 <https://doi.org/10.1016/j.cattod.2018.06.042>.
- 493 [16] Rajesh Banu J, Preethi, Kavitha S, Tyagi VK, Gunasekaran M, Karthikeyan OP, et al.
494 Lignocellulosic biomass based biorefinery: A successful platform towards circular bioeconomy. *Fuel*
495 2021;302:121086. <https://doi.org/10.1016/j.fuel.2021.121086>.
- 496 [17] Reshmy R, Paulose TAP, Philip E, Thomas D, Madhavan A, Sirohi R, et al. Updates on high value
497 products from cellulosic biorefinery. *Fuel* 2022;308:122056.
498 <https://doi.org/10.1016/j.fuel.2021.122056>.

- 499 [18] Cherubini F, Strømman AH. Production of Biofuels and Biochemicals from Lignocellulosic
500 Biomass: Estimation of Maximum Theoretical Yields and Efficiencies Using Matrix Algebra. *Energy Fuels*
501 2010;24:2657–66. <https://doi.org/10.1021/ef901379s>.
- 502 [19] Isikgor FH, Becer CR. Lignocellulosic biomass: a sustainable platform for the production of bio-
503 based chemicals and polymers. *Polymer Chemistry* 2015;6:4497–559.
504 <https://doi.org/10.1039/C5PY00263J>.
- 505 [20] Badgular KC, Badgular VC, Bhanage BM. A review on catalytic synthesis of energy rich fuel
506 additive levulinate compounds from biomass derived levulinic acid. *Fuel Processing Technology*
507 2020;197:106213. <https://doi.org/10.1016/J.FUPROC.2019.106213>.
- 508 [21] Kothe V, Melfi DT, dos Santos KC, Corazza ML, Ramos LP. Thermodynamic analysis,
509 experimental and kinetic modeling of levulinic acid esterification with ethanol at supercritical
510 conditions. *Fuel* 2020;260:116376. <https://doi.org/10.1016/j.fuel.2019.116376>.
- 511 [22] Vilanculo CB, de Andrade Leles LC, da Silva MJ. H4SiW12O40-Catalyzed Levulinic Acid
512 Esterification at Room Temperature for Production of Fuel Bioadditives. *Waste and Biomass*
513 *Valorization* 2020;11:1895–904. <https://doi.org/10.1007/s12649-018-00549-x>.
- 514 [23] Badia JH, Ramírez E, Soto R, Bringué R, Tejero J, Cunill F. Optimization and green metrics
515 analysis of the liquid-phase synthesis of sec-butyl levulinate by esterification of levulinic acid with 1-
516 butene over ion-exchange resins. *Fuel Processing Technology* 2021;220:106893.
517 <https://doi.org/10.1016/j.fuproc.2021.106893>.
- 518 [24] Liu C, Lu X, Yu Z, Xiong J, Bai H, Zhang R. Production of Levulinic Acid from Cellulose and
519 Cellulosic Biomass in Different Catalytic Systems. *Catalysts* 2020;10:1006.
520 <https://doi.org/10.3390/catal10091006>.
- 521 [25] Signoretto M, Taghavi S, Ghedini E, Menegazzo F. Catalytic Production of Levulinic Acid (LA)
522 from Actual Biomass. *Molecules* 2019;24:2760. <https://doi.org/10.3390/molecules24152760>.
- 523 [26] Al Shaal MG. Transformation of Levulinic Acid and Intermediates Thereof into Potential Biofuel
524 Compounds over Heterogeneous Catalysts. RWTH Aachen University, 2016.

- 525 [27] Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule
526 derived from lignocellulosic biomass. *Green Chem* 2013;15:584. <https://doi.org/10.1039/c3gc37065h>.
- 527 [28] van Zandvoort I, Wang Y, Rasrendra CB, van Eck ERH, Bruijninx PCA, Heeres HJ, et al.
528 Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of
529 Feedstock and Processing Conditions. *ChemSusChem* 2013;6:1745–58.
530 <https://doi.org/10.1002/cssc.201300332>.
- 531 [29] Liu R, Chen J, Huang X, Chen L, Ma L, Li X. Conversion of fructose into 5-hydroxymethylfurfural
532 and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials. *Green Chem*
533 2013;15:2895. <https://doi.org/10.1039/c3gc41139g>.
- 534 [30] Yu X, Peng L, Dai J, Li H, Tao C, Yang F, et al. Ethylene glycol co-solvent enhances alkyl levulinate
535 production from concentrated feeds of sugars in monohydric alcohols. *Fuel* 2021;304:121471.
536 <https://doi.org/10.1016/j.fuel.2021.121471>.
- 537 [31] Chang C, Xu G, Zhu W, Bai J, Fang S. One-pot production of a liquid biofuel candidate—Ethyl
538 levulinate from glucose and furfural residues using a combination of extremely low sulfuric acid and
539 zeolite USY. *Fuel* 2015;140:365–70. <https://doi.org/10.1016/j.fuel.2014.09.102>.
- 540 [32] Peng L, Lin L, Zhang J, Shi J, Liu S. Solid acid catalyzed glucose conversion to ethyl levulinate.
541 *Applied Catalysis A: General* 2011;397:259–65. <https://doi.org/10.1016/j.apcata.2011.03.008>.
- 542 [33] An R, Xu G, Chang C, Bai J, Fang S. Efficient one-pot synthesis of n-butyl levulinate from
543 carbohydrates catalyzed by Fe₂(SO₄)₃. *Journal of Energy Chemistry* 2017;26:556–63.
544 <https://doi.org/10.1016/J.JECHEM.2016.11.015>.
- 545 [34] Peng L, Gao X, Chen K. Catalytic upgrading of renewable furfuryl alcohol to alkyl levulinates
546 using AlCl₃ as a facile, efficient, and reusable catalyst. *Fuel* 2015;160:123–31.
547 <https://doi.org/10.1016/J.FUEL.2015.07.086>.
- 548 [35] Peixoto AF, Ramos R, Moreira MM, Soares OSGP, Ribeiro LS, Pereira MFR, et al. Production of
549 ethyl levulinate fuel bioadditive from 5-hydroxymethylfurfural over sulfonic acid functionalized
550 biochar catalysts. *Fuel* 2021;303:121227. <https://doi.org/10.1016/J.FUEL.2021.121227>.

551 [36] Windom BC, Lovestead TM, Mascal M, Nikitin EB, Bruno TJ. Advanced Distillation Curve
552 Analysis on Ethyl Levulinate as a Diesel Fuel Oxygenate and a Hybrid Biodiesel Fuel. *Energy and Fuels*
553 2011;25:1878–90. <https://doi.org/10.1021/EF200239X>.

554 [37] Joshi H, Moser BR, Toler J, Smith WF, Walker T. Ethyl levulinate: A potential bio-based diluent
555 for biodiesel which improves cold flow properties. *Biomass and Bioenergy* 2011;35:3262–6.
556 <https://doi.org/10.1016/J.BIOMBIOE.2011.04.020>.

557 [38] Tian M, McCormick RL, Luecke J, de Jong E, van der Waal JC, van Klink GPM, et al. Anti-knock
558 quality of sugar derived levulinic esters and cyclic ethers. *Fuel* 2017;202:414–25.
559 <https://doi.org/10.1016/J.FUEL.2017.04.027>.

560 [39] Wang Z, Lei T, Lin L, Yang M, Li Z, Xin X, et al. Comparison of the Physical and Chemical
561 Properties, Performance, and Emissions of Ethyl Levulinate–Biodiesel–Diesel and *n*-Butanol–
562 Biodiesel–Diesel Blends. *Energy Fuels* 2017;31:5055–62.
563 <https://doi.org/10.1021/acs.energyfuels.6b02851>.

564 [40] Christensen E, Williams A, Paul S, Burton S, McCormick RL. Properties and Performance of
565 Levulinate Esters as Diesel Blend Components. *Energy and Fuels* 2011;25:5422–8.
566 <https://doi.org/10.1021/EF201229J>.

567 [41] Frigo S, Pasini G, Caposciutti G, Antonelli M, Galletti AMR, Gori S, et al. Utilisation of advanced
568 biofuel in CI internal combustion engine. *Fuel* 2021;297:120742.
569 <https://doi.org/10.1016/J.FUEL.2021.120742>.

570 [42] Di Menno Di Bucchianico D, Wang Y, Buvat J-C, Pan Y, Casson Moreno VC, Leveneur S.
571 Production of levulinic acid and alkyl levulinates: A process insight. *Green Chem* 2021.
572 <https://doi.org/10.1039/D1GC02457D>.

573 [43] Ramírez E, Bringué R, Fité C, Iborra M, Tejero J, Cunill F. Assessment of ion exchange resins as
574 catalysts for the direct transformation of fructose into butyl levulinate. *Applied Catalysis A: General*
575 2021;612:117988. <https://doi.org/10.1016/J.APCATA.2021.117988>.

576 [44] Sun Y, Sun K, Zhang L, Zhang S, Liu Q, Wang Y, et al. Impacts of Solvents on the Stability of the
577 Biomass-Derived Sugars and Furans. *Energy Fuels* 2020;34:3250–61.
578 <https://doi.org/10.1021/acs.energyfuels.9b03921>.

579 [45] Bagno A, Scorrano G. Selectivity in Proton Transfer, Hydrogen Bonding, and Solvation. *Acc*
580 *Chem Res* 2000;33:609–16. <https://doi.org/10.1021/ar990149j>.

581 [46] Guo H, Duereh A, Su Y, Hensen EJM, Qi X, Smith RL. Mechanistic role of protonated polar
582 additives in ethanol for selective transformation of biomass-related compounds. *Applied Catalysis B:*
583 *Environmental* 2020;264:118509. <https://doi.org/10.1016/j.apcatb.2019.118509>.

584 [47] Guo H, Qi X, Hiraga Y, Aida TM, Smith RL. Efficient conversion of fructose into 5-
585 ethoxymethylfurfural with hydrogen sulfate ionic liquids as co-solvent and catalyst. *Chemical*
586 *Engineering Journal* 2017;314:508–14. <https://doi.org/10.1016/j.cej.2016.12.008>.

587 [48] Karnjanakom S, Maneechakr P, Samart C, Guan G. A facile way for sugar transformation
588 catalyzed by carbon-based Lewis-Brønsted solid acid. *Molecular Catalysis* 2019;479:110632.
589 <https://doi.org/10.1016/j.mcat.2019.110632>.

590 [49] Raspolli Galletti AM, Antonetti C, Fulignati S, Licursi D. Direct Alcoholysis of Carbohydrate
591 Precursors and Real Cellulosic Biomasses to Alkyl Levulinates: A Critical Review. *Catalysts*
592 2020;10:1221. <https://doi.org/10.3390/catal10101221>.

593 [50] Iborra M, Tejero J, Fité C, Ramírez E, Cunill F. Liquid-phase synthesis of butyl levulinate with
594 simultaneous water removal catalyzed by acid ion exchange resins. *Journal of Industrial and*
595 *Engineering Chemistry* 2019;78:222–31. <https://doi.org/10.1016/j.jiec.2019.06.011>.

596 [51] Covinich LG, Clauser NM, Felissia FE, Vallejos ME, Area MC. The challenge of converting
597 biomass polysaccharides into levulinic acid through heterogeneous catalytic processes. *Biofuels,*
598 *Bioprod Bioref* 2020;14:417–45. <https://doi.org/10.1002/bbb.2062>.

599 [52] Mellmer MA, Sener C, Gallo JMR, Luterbacher JS, Alonso DM, Dumesic JA. Solvent Effects in
600 Acid-Catalyzed Biomass Conversion Reactions. *Angew Chem Int Ed* 2014;53:11872–5.
601 <https://doi.org/10.1002/anie.201408359>.

602 [53] Wang Y, Cipolletta M, Vernières-Hassimi L, Casson-Moreno V, Leveneur S. Application of the
603 concept of Linear Free Energy Relationships to the hydrogenation of levulinic acid and its
604 corresponding esters. *Chemical Engineering Journal* 2019;374:822–31.
605 <https://doi.org/10.1016/j.cej.2019.05.218>.

606 [54] Capecci S, Wang Y, Delgado J, Casson Moreno V, Mignot M, Grénman H, et al. Bayesian
607 Statistics to Elucidate the Kinetics of γ -Valerolactone from n-Butyl Levulinate Hydrogenation over
608 Ru/C. *Ind Eng Chem Res* 2021;31:11725–36. <https://doi.org/10.1021/acs.iecr.1c02107>.

609 [55] Kerkel F, Markiewicz M, Stolte S, Müller E, Kunz W. The green platform molecule gamma-
610 valerolactone – ecotoxicity, biodegradability, solvent properties, and potential applications. *Green*
611 *Chem* 2021;23:2962–76. <https://doi.org/10.1039/D0GC04353B>.

612 [56] Anastas PT, Warner JC. *Green Chemistry: Theory and Practice*. Oxford University Press: New
613 York; 1998.

614 [57] Srinivas G, Unny VKP, Mukkanti K, Choudary BM. A convenient photosynthesis of uniformly
615 [14C]-labelled d-glucose, d-fructose and sucrose, and chemical synthesis of methyl- α -d-
616 glucopyranoside ([U-14C]-glucose). *Applied Radiation and Isotopes* 2013;72:145–51.
617 <https://doi.org/10.1016/j.apradiso.2012.10.016>.

618 [58] Russo V, Tesser R, Rossano C, Cogliano T, Vitiello R, Leveneur S, et al. Kinetic study of Amberlite
619 IR120 catalyzed acid esterification of levulinic acid with ethanol: From batch to continuous operation.
620 *Chemical Engineering Journal* 2020;401:126126. <https://doi.org/10.1016/J.CEJ.2020.126126>.

621 [59] Altiokka MR, Çıtak A. Kinetics study of esterification of acetic acid with isobutanol in the
622 presence of amberlite catalyst. *Applied Catalysis A: General* 2003;239:141–8.
623 [https://doi.org/10.1016/S0926-860X\(02\)00381-2](https://doi.org/10.1016/S0926-860X(02)00381-2).

624 [60] Jogunola O, Salmi T, Eränen K, Mikkola J-P. Qualitative treatment of catalytic hydrolysis of alkyl
625 formates. *Applied Catalysis A: General* 2010;384:36–44.
626 <https://doi.org/10.1016/j.apcata.2010.06.002>.

627 [61] Mukesh C, Nikjoo D, Mikkola J-P. Production of C-14 Levulinate Ester from Glucose
628 Fermentation Liquors Catalyzed by Acidic Ionic Liquids in a Solvent-Free Self-Biphasic System. ACS
629 Omega 2020;5:4828–35. <https://doi.org/10.1021/acsomega.9b03517>.

630 [62] Leveneur S, Murzin DYu, Salmi T, Mikkola J-P, Kumar N, Eränen K, et al. Synthesis of
631 peroxypropionic acid from propionic acid and hydrogen peroxide over heterogeneous catalysts.
632 Chemical Engineering Journal 2009;147:323–9. <https://doi.org/10.1016/j.cej.2008.11.045>.

633 [63] Bodamer GW, Kunin R. Behavior of Ion Exchange Resins in Solvents Other Than Water -
634 Swelling and Exchange Characteristics. Industrial & Engineering Chemistry 2002;45:2577–80.
635 <https://doi.org/10.1021/IE50527A057>.

636 [64] Bodamer GW, Kunin R. Behavior of Ion Exchange Resins in Solvents Other Than Water -
637 Swelling and Exchange Characteristics. Ind Eng Chem 1953;45:2577–80.
638 <https://doi.org/10.1021/ie50527a057>.

639 [65] Königsberger E. Guidelines for the Measurement of Solid–Liquid Solubility. Journal of Chemical
640 & Engineering Data n.d.;64:381–5. <https://doi.org/10.1021/acs.jced.8b01263>.

641 [66] Engasser J-M, Chamouveau F, Chebil L, Ghoul M. Kinetic modeling of glucose and fructose
642 dissolution in 2-methyl 2-butanol. Biochemical Engineering Journal 2008;42:159–65.
643 <https://doi.org/10.1016/j.bej.2008.06.013>.

644 [67] Flannelly T, Dooley S, Leahy JJ. Reaction Pathway Analysis of Ethyl Levulinate and 5-
645 Ethoxymethylfurfural from D-Fructose Acid Hydrolysis in Ethanol. Energy Fuels 2015;29:7554–65.
646 <https://doi.org/10.1021/acs.energyfuels.5b01481>.

647 [68] Démolis A, Essayem N, Rataboul F. Synthesis and Applications of Alkyl Levulinates. ACS
648 Sustainable Chem Eng 2014;2:1338–52. <https://doi.org/10.1021/sc500082n>.

649 [69] Ahmad E, Alam Mdl, Pant KK, Haider MA. Catalytic and mechanistic insights into the production
650 of ethyl levulinate from biorenewable feedstocks. Green Chem 2016;18:4804–23.
651 <https://doi.org/10.1039/C6GC01523A>.

652 [70] du Toit E, Nicol W. The rate inhibiting effect of water as a product on reactions catalysed by
653 cation exchange resins: formation of mesityl oxide from acetone as case study. *Applied Catalysis A:
654 General* 2004;277:219–25. <https://doi.org/10.1016/j.apcata.2004.09.015>.

655 [71] Pérez MA, Bringué R, Iborra M, Tejero J, Cunill F. Ion exchange resins as catalysts for the liquid-
656 phase dehydration of 1-butanol to di-n-butyl ether. *Applied Catalysis A: General* 2014;482:38–48.
657 <https://doi.org/10.1016/j.apcata.2014.05.017>.

658 [72] Kuo CH, Poyraz AS, Jin L, Meng Y, Pahalagedara L, Chen SY, et al. Heterogeneous acidic TiO₂
659 nanoparticles for efficient conversion of biomass derived carbohydrates. *Green Chem* 2014:785–91.
660 <https://doi.org/10.1039/C3GC40909K>.

661 [73] Balakrishnan M, Sacia ER, Bell AT. Etherification and reductive etherification of 5-
662 (hydroxymethyl)furfural: 5-(alkoxymethyl)furfurals and 2,5-bis(alkoxymethyl)furans as potential bio-
663 diesel candidates. *Green Chem* 2012;14:1626. <https://doi.org/10.1039/c2gc35102a>.

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