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Critical factors for levulinic acid production from starch-rich food waste: Solvent effects, reaction pressure, and phase separation

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1 **Critical factors for levulinic acid production from starch-rich food**
2 **waste: Solvent effects, reaction pressure, and phase separation**

3

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Abstract

A considerable amount of food waste generated globally could be upcycled to synthesise platform chemicals to enhance environmental sustainability and help realise a circular economy. This study investigates the catalytic production of the vital platform molecule levulinic acid (LA) from bread waste, a typical stream of starch-rich food waste generated worldwide. Gamma-valerolactone (GVL), isopropanol (IPA), and propylene carbonate (PC) were evaluated as bio-derived and CO₂-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H₂O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H₂O and IPA/H₂O. In PC/H₂O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H₂SO₄), whereas ~15-20 mol% of LA could be obtained when the reaction was prolonged for 10-20 min at 130°C. The yield of LA could be significantly enhanced in GVL/H₂O through phase separation using NaCl (30 wt%_(aq)). LA yield increased up to a maximum of ~2.5 times in the biphasic system (28 mol%, 150°C, 15 min) (representing a theoretical yield of 66%) in GVL/H₂O (1:1) compared to the monophasic system (~11 mol%) under the same reaction conditions. The partition coefficient for LA achieved was 4.2 in the GVL/H₂O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H₂O facilitated selective LA production, which could be optimised by tuning the reaction conditions. These new insights can foster the development of high-performance LA production and sustainable biorefinery.

Keywords: Waste recycling/management; Platform chemicals; Green solvents; Extractive separation; Sustainably biorefinery; Circular economy.

38 **Introduction**

39 Appropriate and sustainable management of the growing amount of food waste is a big
40 issue in modern society. Approximately 931 million tonnes of food waste were globally generated
41 in the year of 2019 at the retail and consumer level (households and commercial food services),
42 excluding food loss during post-harvest to distribution in the food supply chain.¹ Such an enormous
43 amount of food waste requires proper handling to minimise pollution risks and be diverted from
44 landfill disposal.² Transforming food waste into platform chemicals offers a sustainable
45 opportunity to utilise the vast waste stream for biorefinery applications and pave the way forward
46 to realising a circular bioeconomy.³

47 Levulinic acid (LA) is one of the top bio-derived platform chemicals with various
48 applications, e.g., pharmaceuticals, plasticisers, solvents, fuels, and personal care products.⁴⁻⁵
49 Besides, LA serves as a building block for the production of various value-added derivatives such
50 as gamma-valerolactone (GVL),⁶ succinic acid, diphenolic acid,⁷⁻⁸ alkyl levulinates, 2-methyl-
51 tetrahydrofuran, etc.⁵ Considering the low cost and high catalytic activity for tandem hydrolysis
52 and dehydration reactions, mineral acids such as H₂SO₄ and HCl are generally used for LA
53 production from diverse biomass feedstock including food waste, paper waste, etc.⁹⁻¹⁰ Starch-rich
54 foods such as rice, bread, and potatoes are commonly consumed and constitute a significant
55 proportion of global food waste,¹¹ which can serve as a potential feedstock for biorefineries. Recent
56 studies demonstrated that catalytic production of sugars and platform chemicals could be an
57 effective technique for recycling/valorising a considerable amount of starch-rich food waste
58 generated globally.¹²⁻¹³ In this study, bread waste serves as the representative starch-rich feedstock
59 for the catalytic production of LA.

60 Appropriate reaction conditions and solvent selection are critical for selective and cost-
61 effective LA production.¹⁴ As the greenest and environmentally benign solvent, water has been
62 used as a reaction medium for LA synthesis. However, harsh reaction conditions, i.e., high
63 temperature and acidity, are required when using water as the reaction medium resulting in an
64 energy-intensive process and high byproduct (humin) formation.¹⁵ The selection of a suitable
65 solvent is necessary, as it not only serves as a reaction medium, but also influences the catalytic
66 process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the
67 byproduct formation, etc.^{13,16} Owing to the need for selective and high-efficiency chemical
68 synthesis, various organic solvents as reaction medium have been widely investigated, such as
69 dimethylsulfoxide (DMSO),⁹ tetrahydrofuran (THF), dimethylformamide (DMF),⁷ GVL, acetone,
70 etc.^{10,17} However, conventional organic solvents DMSO, DMF, THF, etc., are widely considered
71 “non-green” due to their direct or indirect detrimental effects on the natural environment and
72 human health and safety. Therefore, the use of alternative “green” solvents, and especially those
73 which are renewable and bio-derived (GVL, alcohols, etc.) or CO₂-derived (propylene carbonate
74 (PC), dimethyl carbonate (DMC), etc.), are recommended for future applications.¹⁸⁻¹⁹ Furthermore,
75 enhanced catalytic conversion of biowaste using these bio-derived and CO₂-derived solvents was
76 reported in recent studies,^{10,13,20} yet their influences should be evaluated in comparable conditions
77 to validate their efficiency and elucidate the critical factors for catalytic LA production.

78 Apart from using environmentally friendly and safe reaction systems, process
79 intensification is indispensable to improve the final concentration of LA for scaling up at the
80 industrial level.¹⁴ Efficient separation and purification of LA are necessary for the possible
81 recovery of mineral acid catalyst and further conversion of LA to valuable derivatives such as
82 GVL, which can be negatively affected by the presence of mineral acid.^{17,21} A viable strategy could

83 be using the biphasic solvent system comprising two immiscible layers. The aqueous layer
84 contains the acid catalyst and serves as the reactive phase, while the organic layer acts as the
85 extractive phase, facilitating simultaneous production and extraction of LA, which might enhance
86 LA yield and selectivity.²¹⁻²² For instance, a recent study on the conversion of remnant algal
87 biomass reported a significant enhancement of hydroxymethylfurfural (HMF) and LA yield using
88 acidic ZSM-5 zeolite as a heterogeneous catalyst when utilising a biphasic solvent system
89 composed of methyl isobutyl ketone (MIBK) and H₂O with NaCl as the phase modifier.²³ Another
90 study achieved a ~4 fold increase in LA yield from rice straw using a biphasic reaction medium
91 containing dichloromethane (DCM) and H₂O (DCM/H₂O, 1:1), in which the enhanced
92 performance was attributed to the good extraction capability of DCM solvent.²⁴ However, there is
93 insufficient experimental evidence and limited understanding of critical impacts of the biphasic
94 system on LA production using the recommended green solvents.

95 This study examines LA production from bread waste using PC, GVL, and isopropanol
96 (IPA) as green co-solvent systems, i.e., PC/H₂O, GVL/H₂O, IPA/H₂O, catalysed by dilute H₂SO₄
97 to investigate how and why an efficient yield of LA could be achieved at moderate reaction
98 conditions using these bio-derived and CO₂-derived green co-solvents. Water (100%) as the
99 greenest solvent was also evaluated as a baseline for comparison. Furthermore, this study explores
100 the application and tuning of the binary biphasic reaction medium to intensify the concentration of
101 the target product LA considering the potential advantages of phase separation for reactive LA
102 extraction.

103 **Materials and methods**

104 **Bread waste and chemicals**

105 Bread waste was collected from catering outlets in the Hong Kong International Airport
106 (HKIA) and dried, ground, sieved through a 0.3 mm mesh, and stored in an airtight container for
107 further experimental use. The bread waste contains 72.6% available carbohydrates, 4.2% total
108 dietary fibre, 14.8% protein, 6.1% total fat, 2.3% ash, and 41.5% total organic carbon (TOC) on a
109 dry mass basis.¹³ Solvents were purchased as follows, PC (99%, Aladdin), IPA (99%, Honeywell),
110 and GVL (99%, Sigma-Aldrich). The standard chemical/compounds for calibration of the
111 analytical equipment and catalytic reaction included glucose (99%, UNI-chem, China); fructose
112 ($\geq 99\%$) and maltose monohydrate (98%) (WAKO); levoglucosan (LG) (Fluorochem); LA (98%),
113 and formic acid (FA) (98%) (Alfa Aesar); furfural (99%) and HMF ($\geq 99\%$, Sigma Aldrich); and
114 H_2SO_4 (98%, Honeywell Fluka). All standard chemicals were used as received.

115 **Catalytic conversion**

116 The catalytic conversion of bread waste substrate was performed under microwave heating
117 in a microwave reactor (Ethos Up Microwave Reactor, Milestone, maximum power of 1.9 kW)
118 following the method reported in our recent studies.^{13,20} To perform catalytic tests using a
119 monophasic system, 0.5 g bread waste (5 wt/v%), a mixture of organic solvent (PC/GVL/IPA) and
120 water (total volume 10 ml; solvent ratio 1:1 for monophasic reaction), and 0.5 M H_2SO_4 were
121 loaded in Teflon vessel and sealed, then heated to reach the desired reaction temperature (110-
122 150°C) following a constant ramp rate (32°C min⁻¹), followed by a holding stage for 1-20 min, and
123 cooling down for 20-30 min using mechanical ventilation. Each experimental run was conducted
124 in duplicates to ensure reliable analysis. The reaction conditions were selected based on the latest
125 studies on starch-rich food waste conversion^{11,13} and adjusted if necessary based on the

126 experimental observations. To substantiate the experimental results obtained in PC/H₂O solvent,
127 additional tests under the selected conditions were conducted using propylene glycol (PG) and
128 water (PG/H₂O, 1:1) for comparison.

129 After analysing the results obtained from different monophasic solvent systems, GVL/H₂O
130 and IPA/H₂O solvents were investigated for biphasic reactions. As GVL and IPA are completely
131 miscible in water, 30 wt%_(aq) NaCl was applied as a phase modifier to prepare the biphasic
132 system,^{21,25} and catalytic tests were conducted following the conditions mentioned above. It is
133 noted that the concentration of H₂SO₄ refers to the whole solvent system (i.e., consistent for all
134 experimental runs with different solvents, both monophasic and biphasic), whereas the
135 concentration of NaCl refers to the reaction phase only, which is denoted as NaCl_(aq). To analyse
136 the influence of the reaction phase and extraction phase on catalytic performance in the biphasic
137 system, different ratios of water and organic solvent (1:1, 1:3, 3:1) were applied for the conversion.
138 Control runs without bread waste substrate were performed for solvent systems under the selected
139 conditions. Standard thermocouple and pressure data-logger were used during catalytic reactions
140 to monitor and record the in-vessel reaction temperature and autogenous pressure, respectively.

141 **Analysis of samples**

142 Soluble samples were obtained from each replicate, diluted with deionised water (DIW),
143 and filtered through a membrane filter (0.45 µm) before analysis. For biphasic reactions, samples
144 were obtained from each layer and prepared separately for analysis after dilution in DIW. High-
145 performance liquid chromatography (HPLC) consisting of a Chromaster instrument equipped with
146 Aminex HPX-87H column (Bio-Rad) and a refractive index detector (Hitachi, Japan) was used to
147 analyse the soluble products; 0.01 M H₂SO₄ was used as the mobile phase at 0.5 ml min⁻¹ flow rate
148 at 50 °C.^{10,26} To ensure reliable analysis, spiked samples with known concentrations of standard

149 compounds were injected before analysing the experimental samples. The yield of products was
150 calculated based on the carbon content (Eq. (1)) of the bread waste substrate.¹³

$$151 \quad \text{Product yield (C mol\%)} = \frac{\text{Conc}_p (\text{mg ml}^{-1}) \times \text{Vol (ml)} / \text{MW}_p \times C_p}{C_s (\text{mol})} \times 100 \quad (1)$$

152 Where Conc_p denotes the concentration of products (including disaccharide, glucose, fructose, LG,
153 HMF, LA, FA, and furfural); MW_p and C_p represent the molecular mass and number of carbons in
154 the related product, respectively; C_s represents the total number of organic carbons in the substrate,
155 which is 17.3 mmol for 0.5 g of bread waste. A volume loss of 5-15% (following various reaction
156 duration) was recorded for PC/H₂O solvent, which was taken into account for calculating the
157 soluble product yields. For biphasic systems, partition coefficients (R_x) for a particular product
158 such as LA (R_{LA}) and FA (R_{FA}) were calculated following Eq. (2),

$$159 \quad \text{Partition coefficient } (R_x) = \frac{\text{C mol\% of product in the organic layer}}{\text{C mol\% of product in the aqueous layer}} \quad (2)$$

160 Post-reaction solid residues were collected through centrifugation and decantation; washed
161 with DIW three times and oven-dried for 48 h at 60°C and then ground as a powder for further
162 analysis using ¹³C nuclear magnetic resonance (NMR). Solid ¹³C NMR were recorded with bulk
163 powder samples on a Jeol JNM-ECZ500R MHz spectrometer operating at a resonance frequency
164 of 125 MHz. A commercial 3.2 mm magic-angle spinning (MAS) NMR probe was used with a
165 standard cross-polarisation MAS (CPMAS) pulse sequence. The MAS frequency was 10 kHz with
166 relaxation delay, scan times, and contact time at 5 s, 1200-2000, and 2 ms, respectively. Liquid
167 samples subjected to the selected reaction conditions were also analysed by ¹³C NMR using D₂O
168 solution. Chemical shifts (δ) were given in ppm and measured relative to tetramethylsilane (TMS)
169 as the internal standard. The solid residues were also characterised by X-ray diffraction (XRD)

170 (Rigaku Smatlab, 5° to 50° 2θ , rate: $10^\circ \text{ min}^{-1}$ at 45 kV and 200 mA) and the crystallinity index
171 (CrI) was calculated from XRD patterns following the method reported in the literature.²⁷

172 **Results and discussion**

173 **Catalytic conversion of bread waste under bio-derived and CO₂-derived solvents**

174 Facile conversion of bread waste was achieved under moderate reaction conditions,
175 obtaining 45-72 mol% total product yield at 130°C under bio-derived and CO₂-derived co-solvent
176 systems (**Fig. 1a**). For H₂O, PC/H₂O, and GVL/H₂O solvents, the maximum total sugars released
177 from bread waste were 64-70 mol% in a short reaction duration of 1 min (**Fig. S1a**). In contrast,
178 using IPA/H₂O, the total sugar yield after 1 min of reaction was 43.5 mol%, increasing up to 48.8
179 mol% when the reaction was prolonged for 20 min. Given the total sugar yield generated at 110°C
180 (**Fig. 1b**), hydrolysis of bread waste was faster in GVL/H₂O (48.1 mol%) and PC/H₂O (53.7 mol%)
181 compared to H₂O (~30 mol%) and IPA/H₂O (9.4 mol%). With increasing reaction duration up to
182 20 min, sugar yield in H₂O and IPA/H₂O remained steady and generated an insignificant LA yield
183 ~1.5 mol% after 20 min of reaction. In contrast, sugars were consumed, and LA yield increased
184 with increasing reaction duration gradually in GVL/H₂O (up to 4.8 mol%) and sharply in PC/H₂O
185 (up to 19.6 mol%) (**Fig. 1a**). ¹³C NMR spectra of reacted solutions (1 and 20 min reaction) (**Fig.**
186 **2a**) provided further evidence for the disparity in catalytic conversion under different solvent
187 systems. ¹³C NMR chemical shift (δ) at 95.8 ppm, attributed to glucose,²⁸ was observed for all
188 reactions. The highest intensity of glucose peak was observed for 1 min reacted solution in
189 PC/H₂O, which agrees with the maximum sugar yield measured by HPLC. In contrast, the lowest
190 intensity of glucose peak and emerged LA peak (at 27.7, 37.6, 177 pm) along with an FA peak (at
191 165.45 ppm)²⁹ for 20 min reaction in PC/H₂O further prove the efficient tandem catalysis in
192 PC/H₂O. The characteristic peaks for LA and FA were not detectable in IPA/H₂O and H₂O, while

193 low-intensity peaks could be observed for GVL/H₂O. Besides, representative solvent peaks²⁹ were
194 detected in the reacted solutions indicated in **Fig. 2a**.

195 The higher soluble product yields in PC/H₂O and GVL/H₂O (**Fig. 1b**) could be related to
196 the high reactivity of the Brønsted acid catalyst due to the availability of highly active proton in
197 the presence of aprotic co-solvents in the reaction system.^{13,30} The extent of proton stabilisation
198 influences the acid dissociation constant, and in water lowers the proton reactivity, which
199 subsequently elevates the required energy level for acid-catalysed biomass conversion reactions
200 such as hydrolysis and dehydration.³⁰ Therefore, reaction kinetics could be slower in H₂O (100%)
201 compared to a solvent system consisting of a polar aprotic solvent such as GVL and PC, which
202 might enhance the reaction rates owing to reactive proton and facile glycosidic bond cleavage.^{20,31}
203 For instance, a recent study reported a ten-fold increase in reaction rate for acid-catalysed
204 conversion of HMF to LA using GVL with 10% H₂O compared to 100% H₂O as solvent.³² Slower
205 conversion of bread waste was observable in the case of IPA/H₂O solvent (total sugar ~10 mol%,
206 at 110°C, 1 min) (**Fig. 1b**), where both co-solvents are protic and probably hamper the proton
207 reactivity during conversion.

208 The starch contained in the bread waste substrate represents a complex structure combining
209 linear amylose chains and highly branched amylopectin comprising $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$
210 glycosidic bonds. ¹³C NMR spectra of solid residues (**Fig. 2b**) subjected to reaction under different
211 solvent systems (20 min) showed differences in chemical shifts than the untreated bread waste,
212 possibly related to the changes in starch structures.³³ The chemical shifts observed at resonance
213 values of 93-103, 74-85, 64-73, 55-60 ppm can be attributed to C1, C4, C2,3,5, and C6 of glucose
214 units, respectively.^{11,34} Resonance values attributed to C1 and C4 can be helpful to understand the
215 changes in the amorphous and highly ordered/crystalline state of starch. The C1 resonance for

216 post-reaction solid residues shifted toward 98-103 ppm, presenting comparatively sharp peaks
217 compared to the broad peak observed at 93-100 ppm for untreated bread waste. The broad shoulder
218 observed around 95 ppm for untreated bread waste is characteristic of the amorphous domain of
219 C1. In contrast, a sharp peak observed around 100 ppm (C1) for solid residues might indicate a
220 decrease in amorphous content and a subsequent rise in relative crystallinity, which was previously
221 reported for acid-modified starch.³⁴⁻³⁵ In contrast, the resonance for C4 around 82 ppm was
222 observed for solid residues, characteristic of an amorphous state.³⁶ Different changes in chemical
223 shifts in different carbon regions can reflect varied transformations between amylose and
224 amylopectin within the starch structures. Amylose is mainly amorphous and more susceptible to
225 acid hydrolysis than amylopectin, which comprises highly ordered/crystalline domain building
226 double-helical structures. However, initially during acid hydrolysis, amorphous amylose could be
227 partially transformed into double helices resistant to acid hydrolysis, and consequently, crystalline
228 content could be enhanced relative to amorphous content.³⁷⁻³⁸ The observed changes in solid
229 residues compared to untreated bread waste was substantiated by XRD analysis. The XRD pattern
230 of untreated bread waste (**Fig. S2**) showed a broad crystalline peak at $\sim 2\theta=20^\circ$, and the calculated
231 *CrI* value was ~ 0.51 , whereas solid residues in different solvent systems provided *CrI* values
232 ranging $\sim 0.73-0.78$. This also suggested the rapid decomposition of amorphous region of starch
233 granules during acid hydrolysis resulting in an increased relative crystallinity.²⁷

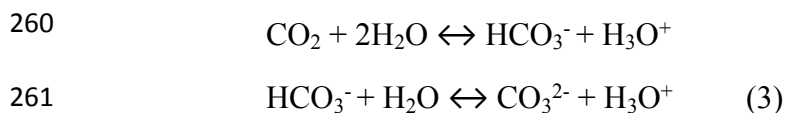
234

235 **LA yield enhanced by in-vessel high pressure generated in PC/H₂O**

236 Comparing different co-solvent systems, PC/H₂O was found to be the best for LA
237 production, generating 19.6 mol% after 20 min reaction at 130°C (**Fig. 1a**), which is promising
238 considering mild reaction conditions used in this study and the reported literature results under
239 comparable experimental conditions.^{9,39} Under GVL/H₂O solvent, sugars depleted gradually
240 during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H₂O solvent, sugars
241 started to deplete rapidly during 3-20 min of reaction, and 19.6 mol% LA yield was achieved after
242 20 min. A significant in-vessel pressure build-up was recorded during reaction in PC/H₂O,
243 reaching a maximum ~27 bar at 130°C, 20 min compared to reactions in other solvents (**Fig. 3a**).
244 Compared to the autogenous in-vessel pressure (~13 bar) generated in PC/H₂O during 1 min
245 reaction, the reaction pressure level almost doubled (~23-27 bar) during 3-20 min reaction (**Fig.**
246 **3b**), which was analogous to rapid sugar consumption and a sharp increase in LA yield (4-19.6
247 mol%) during 3-20 min. In acidic conditions, PC solvent could decompose into PG and CO₂ as
248 reported in the literature.^{13,40} Noticeably, ~5-15% solvent loss was recorded for reactions in
249 PC/H₂O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the
250 reaction. Besides, ¹³C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H₂O (1 and 20
251 min) showed peaks at 66.4 and 67.7 ppm representing PG.²⁹ The PG peaks had comparatively
252 higher intensity after 20 min reaction than 1 min, suggesting that a higher fraction of PC was
253 decomposed to PG, which was consistent with higher CO₂ pressure recorded for more prolonged
254 reactions in PC/H₂O (**Fig. 3b**).

255 Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from
256 CO₂ generation during catalytic conversion in PC/H₂O might enhance the LA production rate.
257 Another influential factor could be the increased acidity due to carbonic acid derived from partial

258 dissolution of CO₂ during the reaction, which might enhance sugar dehydration.⁴¹ Solution acidity
259 can arise through *in situ* formation and dissociation of carbonic acid, as given in Eq. (3).⁴²



262 The acidity (pH) associated with CO₂ generated during 3-20 min reaction in PC/H₂O was
263 estimated, following the scheme reported in the literature.⁴³⁻⁴⁴ The estimated CO₂-derived pH
264 value for specified reaction conditions was ~3.5, i.e., considerably higher than the H₂SO₄ derived
265 pH (~0.5) in this study. Therefore, CO₂-derived pH on its own might not be sufficient to catalyse
266 tandem reactions and significantly enhance LA yield. In other words, LA yield might be improved
267 probably by PC/H₂O generated CO₂ pressure more than CO₂-derived acidity during the catalytic
268 conversion of bread waste. To testify this postulation, an additional test using PC/H₂O was
269 conducted, in which autogenous pressure developed due to PC degradation (~22 bar) was released
270 after 5 min reaction, and then the solution underwent reaction for another 15 min (**Fig. 3c**).
271 Compared to continuous 20 min reaction in PC/H₂O (LA yield 19.6 mol%), only about half of LA
272 was produced (LA yield 11.2 mol%) when the pressure was released prematurely during the
273 reaction. After the pressure release, the autogenous pressure was ~4.2 bar from the beginning till
274 the end point of additional 15-min reaction. Moreover, supplementary tests using PG/H₂O only
275 generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA
276 yield obtained in PC/H₂O, therefore disproving any favourable influences by PG solvent
277 (decomposed from PC) on the catalytic performance. These experimental evidences confirm the
278 crucial enhancement of reaction pressure on the catalytic LA production.

279 Intensification of LA yield through phase separation

280 Among co-solvent systems, PC/H₂O generated the highest LA yield 19.6 mol% at 130°C, and
281 ~9 mol% soluble sugar remained after a 20 min reaction. In contrast, ~47-49 mol% soluble sugar
282 was available after 20 min reaction in GVL/H₂O and IPA/H₂O (**Fig. 1a**), which could be further
283 converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H₂O
284 and IPA/H₂O, conversion of bread waste was conducted at 150°C for 1-20 min reaction duration
285 (**Fig. 4a&b**). As higher temperature provided more energy for the reaction, LA yield increased
286 gradually up to 16.4 mol% in GVL/H₂O (150°C, 20 min) (**Fig. 4b**), which was more than three
287 times higher than the maximum LA yield achieved at 130°C (4.8 mol%, 20 min). The maximum
288 LA yield achieved in IPA/H₂O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than
289 GVL/H₂O system, corroborating the positive role of aprotic GVL solvent in enhancing proton
290 reactivity for less energy-intensive tandem catalysis.^{10,30}

291 The biphasic solvent systems (prepared using 30 wt% NaCl_(aq)) were further investigated
292 as an intensification scheme to improve the concentration of the target product LA in this study.
293 Promisingly, the concentration of LA at the end of the reaction (150°C, 20 min) increased ~1.6
294 times in both biphasic GVL/H₂O and IPA/H₂O systems (**Fig. 4c**) compared to analogous
295 monophasic systems. Though total soluble product yields were comparable in the two biphasic
296 systems (~33-35 mol%) (**Fig. S1b**), the distributions of soluble products were distinctive between
297 GVL/H₂O and IPA/H₂O. While biphasic GVL/H₂O selectively generated LA as the main product
298 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H₂O biphasic contained 10.6 mol% LA, 2.6
299 mol% FA, ~7 mol% HMF, and 10.2 mol% remaining sugars (glucose and fructose) (**Fig. 4c**). A
300 considerable fraction of HMF present in both monophasic and biphasic IPA/H₂O indicated that
301 the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely

302 recommended solvent for HMF production, IPA can create a shielding effect around HMF that
303 helps to prevent its rehydration and suppress further conversion to byproducts such as insoluble
304 humins.⁴⁵⁻⁴⁶ A recent study revealed that the rate constant for fructose to HMF was considerably
305 higher than that of HMF to degradation products when IPA was present in the solvent system,⁴⁶
306 echoing the experimental observations in this study where low LA selectivity was obtained in
307 IPA/H₂O solvent system. In other words, IPA/H₂O could be considered as a potential solvent for
308 HMF production in future investigations. By contrast, in the presence of GVL solvent, H₂SO₄
309 catalysed HMF production could be rapid and readily converted to LA at high acid strength.⁴⁷
310 Considerable LA yield achieved in biphasic GVL/H₂O in this study (26.8 mol%, at 150°C, 20 min)
311 proves the high efficiency of H₂SO₄/GVL/H₂O system for LA production.

312 As GVL/H₂O biphasic solvent was the most efficient for intensifying LA yield at moderate
313 conditions, a comprehensive investigation was conducted for bread waste conversion in the co-
314 solvent system following varied reaction conditions (150°C, 10-20 min). In biphasic GVL/H₂O,
315 LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H₂O,
316 1:1) (**Fig. 5a**). However, a slight decrease in LA yield was observed after 20 min, suggesting that
317 LA started to degrade with prolonged reaction. The major product in monophasic GVL/H₂O (1:1,
318 15 min) was glucose (34.6 mol%), while the biphasic system selectively generated LA (~28 mol%)
319 as the major product. The LA yield increased up to ~2.5 times in the biphasic system compared to
320 the monophasic one (~11 mol%) (150°C, 15 min), implying that phase separation could be
321 beneficial for intensive LA production and upscaling to industrial scale.

322 Essentially, to develop an efficient biphasic reaction medium, it is necessary to understand
323 the contribution and influences of the reaction phase (H₂O) and the extraction phase (GVL) to
324 optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H₂O

325 biphasic system, catalytic tests were conducted with various ratios of GVL and H₂O (1:1, 1:3, and
326 3:1 of GVL/H₂O). The partition coefficient for LA (R_{LA}) in the GVL/H₂O biphasic solvent was
327 calculated to evaluate the effect of the extraction phase (GVL) in the system. The R_{LA} achieved for
328 10-15 min reaction was 4.2 when 1:1 GVL/H₂O was applied for reaction (**Fig. 5b**), indicating a
329 higher distribution of LA in the organic phase compared to the aqueous phase. Therefore, GVL
330 solvent can be considered highly effective for reactive LA extraction. The partitioning of LA
331 obtained in this study (R_{LA} 4.2) is comparable to a previous study that reported R_{LA} ranging 3.7-4
332 using cellulose as feedstock.²¹

333 The total yield of LA increased (27.4-32 mol%) when a higher fraction of H₂O (1:3,
334 GVL/H₂O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-
335 17.1 mol%) when a lower fraction of H₂O (3:1, GVL/H₂O) was applied (**Fig. 5b**). Though the total
336 LA yield increased with a higher fraction of H₂O, the extraction of LA was found to be inefficient.
337 The partition coefficient achieved was only 1.1 (1:3, GVL/H₂O), indicating nearly even
338 distribution of produced LA in the reaction and extraction phases due to the lower fraction of GVL
339 applied. In comparison, ~97% of the total LA produced was extracted into the GVL phase when a
340 higher fraction of GVL (3:1, GVL/H₂O) was applied for reaction. However, a considerable
341 decrease in total LA yield was observed, possibly due to the lack of sufficient aqueous phase
342 available for reaction. These observations suggested the indispensable contribution of both
343 reaction and extraction phases for an efficient biphasic system for LA production. Considering LA
344 yield (27.4 mol%) and R_{LA} (4.2), the 1:1 GVL/H₂O biphasic system (150°C, 15 min) provided the
345 best performance for intensive LA production.

346 To reflect further on the mechanism and roles of catalytic species in NaCl modified
347 GVL/H₂O biphasic system, additional tests were performed under the selected reaction conditions.

348 In the case of reaction conducted with only NaCl (30 wt%) without acid catalyst, only marginal
349 product yield was observed (**Fig. 6a**). When NaCl was applied together with H₂SO₄ for bread
350 waste conversion, an increase in LA yield was observed compared to the reaction in the presence
351 of H₂SO₄ without salt addition. These observations indicate that NaCl alone could not catalyse the
352 desired reaction yet it may act synergistically with H₂SO₄ enhancing the LA production in the
353 aqueous phase during biphasic conversion of bread waste. Product distributions in the aqueous and
354 GVL phases in the specified reaction conditions are provided in **Fig. S3**. The synergistic catalysis
355 by NaCl and H₂SO₄ together with simultaneous efficient extraction of LA into GVL could account
356 for the high LA yield obtained in the GVL/H₂O biphasic system.

357 Moreover, the recyclability of the aqueous phase containing H₂SO₄ was investigated. After
358 the catalytic run (reaction and cooling), the reacted organic phase was removed and fresh GVL
359 and bread waste substrate were applied for another cycle of catalytic reaction (run-2) again while
360 retaining the aqueous phase from the previous run without adding extra H₂SO₄. Similarly, the third
361 cycle of catalytic reaction (run-3) was conducted. In the 2nd and 3rd run (**Fig. 6b**), 15 mol% and 13
362 mol% LA was obtained, respectively, compared to the LA yield (28 mol%) obtained in the initial
363 run, which suggested that the acid catalyst could be retained in the aqueous phase and recycled for
364 further conversion, though a certain degree of decrease in LA yield was observed. Future studies
365 would be required for evaluating the biphasic system in a continuous reaction mode, which may
366 be more efficient compared to the batch reaction mode.

367 Apart from LA as the target product, FA yield was analysed for bread waste conversion in
368 monophasic and biphasic GVL/H₂O, as FA is often co-produced during biomass conversion.⁴⁸
369 Similar to LA, the FA yield was enhanced through phase separation with the yield from ~2-3 mol%
370 in the monophasic system to a maximum 5.4 mol% FA yield in biphasic GVL/H₂O (150°C, 15

371 min, 1:3 solvent ratio) (**Fig. 5c**). Using 1:1 GVL/H₂O, FA partition coefficient (R_{FA}) obtained was
372 ~2-3 (150°C, 10-20 min, solvent ratio 1:1) (**Fig. 5c**), indicating that FA could also be
373 simultaneously extracted into the GVL layer during bread waste conversion. Besides, partition
374 coefficients for LA, FA, and HMF were evaluated in IPA/H₂O solvent (150°C, 20 min, 1:1 solvent
375 ratio), and the values were 6.6, 5.4, and 5.7, respectively (**Fig. S4**), corroborating an effective
376 extraction of these compounds into the organic phase. Considering the low LA selectivity and total
377 LA yield (10.6 mol% at 150°C, 20 min), further investigation was discontinued for IPA/H₂O.

378 **Perspectives on LA production and solvent recycling**

379 To evaluate the efficiency of the catalytic system for LA production, LA yield relative to
380 theoretical LA yield of bread waste substrate (considering total available carbohydrate and
381 possible maximum theoretical yield (64.5%)) was calculated and compared with the reported
382 achievements with commercially available starch substrates in the existing literature (**Table 1**).
383 For PC/H₂O (130°C, 20 min) and GVL/H₂O biphasic solvents (150°C, 15 min), 45.7% and 66%
384 LA yield was achieved relative to theoretical yield, respectively. This is considered promising in
385 comparison to the reported LA yield (45.6-66.4%) from commercially available starch substrates
386 in previous studies⁴⁹⁻⁵⁰ where the conversion was conducted using comparatively harsh reaction
387 conditions. For other recent studies where no direct comparison is possible due to the lack of data
388 regarding relative LA yield,^{17,51} it should be noted that much longer reaction duration was required
389 to obtain the reported LA yield.

390 The recyclability of GVL/H₂O biphasic solvent was investigated and discussed in the
391 previous section. For PC/H₂O solvent, despite partial decomposition of PC during acid catalysis,
392 it offers various advantages as a solvent because a high product yield can be obtained with a
393 moderate temperature and a short duration, which play a critical role in reducing the energy

394 consumption and reactor size. The production of PC from CO₂ is beneficial for process economy
395 and environmental sustainability in terms of CO₂ utilisation. In the application of PC solvent, the
396 derived CO₂ after reaction can be captured and recycled for PC production or other CO₂ based
397 biorefineries, which are conducive to fostering the circular economy. The spent organic solvents
398 can be recycled after separation and purification following commonly used techniques such as
399 fractional distillation. For instance, a comprehensive life cycle assessment (LCA) on solvent waste
400 recovery⁵² demonstrated that implementing a solvent recovery system can reduce the
401 environmental footprint of the total solvent manufacturing, usage, and disposal process. The
402 energy requirements and emissions associated with the solvent recovery process have been
403 recognised to be trivial in comparison to the emissions due to virgin solvent production and spent
404 solvent disposal by incineration.

405 **Conclusions**

406 This study provides comprehensive insights into the critical factors for intensive LA
407 production, which can be conducive to the technology scale-up. The bio-derived and CO₂-derived
408 co-solvents in this study, i.e., PC/H₂O, GVL/H₂O, IPA/H₂O, could facilitate H₂SO₄ catalysed
409 tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency.
410 PC/H₂O solvent was the most efficient for LA production using moderate reaction conditions,
411 which could be attributed to the CO₂ pressure generated *in situ* through solvent (PC) degradation.
412 Besides, catalytic performance could be significantly enhanced in GVL/H₂O and IPA/H₂O using
413 the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the
414 final concentration of LA. GVL/H₂O biphasic solvent seems promising considering LA yield (28
415 mol%) and LA partitioning (R_{LA} 4.2) achieved in the study. The bio-derived and CO₂-derived

416 solvents applied in this study can be considered as emerging solvents and potential alternatives to
417 common industrial solvents in future biorefinery applications.

418

419 **Supplementary information**

420 The supplementary information is available online.

421

422 **Conflicts of interest**

423 The authors declare no conflict of interest.

424

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1 **Critical factors for levulinic acid production from starch-rich food**
2 **waste: Solvent effects, reaction pressure, and phase separation**

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Abstract

A considerable amount of food waste generated globally could be upcycled to synthesise platform chemicals to enhance environmental sustainability and help realise a circular economy. This study investigates the catalytic production of the vital platform molecule levulinic acid (LA) from bread waste, a typical stream of starch-rich food waste generated worldwide. Gamma-valerolactone (GVL), isopropanol (IPA), and propylene carbonate (PC) were evaluated as bio-derived and CO₂-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H₂O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H₂O and IPA/H₂O. In PC/H₂O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H₂SO₄), whereas ~15-20 mol% of LA could be obtained when the reaction was prolonged for 10-20 min at 130°C. The yield of LA could be significantly enhanced in GVL/H₂O through phase separation using NaCl (30 wt%_(aq)). LA yield increased up to a maximum of ~2.5 times in the biphasic system (28 mol%, 150°C, 15 min) (representing a theoretical yield of 66%) in GVL/H₂O (1:1) compared to the monophasic system (~11 mol%) under the same reaction conditions. The partition coefficient for LA achieved was 4.2 in the GVL/H₂O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H₂O facilitated selective LA production, which could be optimised by tuning the reaction conditions. These new insights can foster the development of high-performance LA production and sustainable biorefinery.

Keywords: Waste recycling/management; Platform chemicals; Green solvents; Extractive separation; Sustainably biorefinery; Circular economy.

38 **Introduction**

39 Appropriate and sustainable management of the growing amount of food waste is a big
40 issue in modern society. Approximately 931 million tonnes of food waste were globally generated
41 in the year of 2019 at the retail and consumer level (households and commercial food services),
42 excluding food loss during post-harvest to distribution in the food supply chain.¹ Such an enormous
43 amount of food waste requires proper handling to minimise pollution risks and be diverted from
44 landfill disposal.² Transforming food waste into platform chemicals offers a sustainable
45 opportunity to utilise the vast waste stream for biorefinery applications and pave the way forward
46 to realising a circular bioeconomy.³

47 Levulinic acid (LA) is one of the top bio-derived platform chemicals with various
48 applications, e.g., pharmaceuticals, plasticisers, solvents, fuels, and personal care products.⁴⁻⁵
49 Besides, LA serves as a building block for the production of various value-added derivatives such
50 as gamma-valerolactone (GVL),⁶ succinic acid, diphenolic acid,⁷⁻⁸ alkyl levulinates, 2-methyl-
51 tetrahydrofuran, etc.⁵ Considering the low cost and high catalytic activity for tandem hydrolysis
52 and dehydration reactions, mineral acids such as H₂SO₄ and HCl are generally used for LA
53 production from diverse biomass feedstock including food waste, paper waste, etc.⁹⁻¹⁰ Starch-rich
54 foods such as rice, bread, and potatoes are commonly consumed and constitute a significant
55 proportion of global food waste,¹¹ which can serve as a potential feedstock for biorefineries. Recent
56 studies demonstrated that catalytic production of sugars and platform chemicals could be an
57 effective technique for recycling/valorising a considerable amount of starch-rich food waste
58 generated globally.¹²⁻¹³ In this study, bread waste serves as the representative starch-rich feedstock
59 for the catalytic production of LA.

60 Appropriate reaction conditions and solvent selection are critical for selective and cost-
61 effective LA production.¹⁴ As the greenest and environmentally benign solvent, water has been
62 used as a reaction medium for LA synthesis. However, harsh reaction conditions, i.e., high
63 temperature and acidity, are required when using water as the reaction medium resulting in an
64 energy-intensive process and high byproduct (humin) formation.¹⁵ The selection of a suitable
65 solvent is necessary, as it not only serves as a reaction medium, but also influences the catalytic
66 process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the
67 byproduct formation, etc.^{13,16} Owing to the need for selective and high-efficiency chemical
68 synthesis, various organic solvents as reaction medium have been widely investigated, such as
69 dimethylsulfoxide (DMSO),⁹ tetrahydrofuran (THF), dimethylformamide (DMF),⁷ GVL, acetone,
70 etc.^{10,17} However, conventional organic solvents DMSO, DMF, THF, etc., are widely considered
71 “non-green” due to their direct or indirect detrimental effects on the natural environment and
72 human health and safety. Therefore, the use of alternative “green” solvents, and especially those
73 which are renewable and bio-derived (GVL, alcohols, etc.) or CO₂-derived (propylene carbonate
74 (PC), dimethyl carbonate (DMC), etc.), are recommended for future applications.¹⁸⁻¹⁹ Furthermore,
75 enhanced catalytic conversion of biowaste using these bio-derived and CO₂-derived solvents was
76 reported in recent studies,^{10,13,20} yet their influences should be evaluated in comparable conditions
77 to validate their efficiency and elucidate the critical factors for catalytic LA production.

78 Apart from using environmentally friendly and safe reaction systems, process
79 intensification is indispensable to improve the final concentration of LA for scaling up at the
80 industrial level.¹⁴ Efficient separation and purification of LA are necessary for the possible
81 recovery of mineral acid catalyst and further conversion of LA to valuable derivatives such as
82 GVL, which can be negatively affected by the presence of mineral acid.^{17,21} A viable strategy could

83 be using the biphasic solvent system comprising two immiscible layers. The aqueous layer
84 contains the acid catalyst and serves as the reactive phase, while the organic layer acts as the
85 extractive phase, facilitating simultaneous production and extraction of LA, which might enhance
86 LA yield and selectivity.²¹⁻²² For instance, a recent study on the conversion of remnant algal
87 biomass reported a significant enhancement of hydroxymethylfurfural (HMF) and LA yield using
88 acidic ZSM-5 zeolite as a heterogeneous catalyst when utilising a biphasic solvent system
89 composed of methyl isobutyl ketone (MIBK) and H₂O with NaCl as the phase modifier.²³ Another
90 study achieved a ~4 fold increase in LA yield from rice straw using a biphasic reaction medium
91 containing dichloromethane (DCM) and H₂O (DCM/H₂O, 1:1), in which the enhanced
92 performance was attributed to the good extraction capability of DCM solvent.²⁴ However, there is
93 insufficient experimental evidence and limited understanding of critical impacts of the biphasic
94 system on LA production using the recommended green solvents.

95 This study examines LA production from bread waste using PC, GVL, and isopropanol
96 (IPA) as green co-solvent systems, i.e., PC/H₂O, GVL/H₂O, IPA/H₂O, catalysed by dilute H₂SO₄
97 to investigate how and why an efficient yield of LA could be achieved at moderate reaction
98 conditions using these bio-derived and CO₂-derived green co-solvents. Water (100%) as the
99 greenest solvent was also evaluated as a baseline for comparison. Furthermore, this study explores
100 the application and tuning of the binary biphasic reaction medium to intensify the concentration of
101 the target product LA considering the potential advantages of phase separation for reactive LA
102 extraction.

103 **Materials and methods**

104 **Bread waste and chemicals**

105 Bread waste was collected from catering outlets in the Hong Kong International Airport
106 (HKIA) and dried, ground, sieved through a 0.3 mm mesh, and stored in an airtight container for
107 further experimental use. The bread waste contains 72.6% available carbohydrates, 4.2% total
108 dietary fibre, 14.8% protein, 6.1% total fat, 2.3% ash, and 41.5% total organic carbon (TOC) on a
109 dry mass basis.¹³ Solvents were purchased as follows, PC (99%, Aladdin), IPA (99%, Honeywell),
110 and GVL (99%, Sigma-Aldrich). The standard chemical/compounds for calibration of the
111 analytical equipment and catalytic reaction included glucose (99%, UNI-chem, China); fructose
112 ($\geq 99\%$) and maltose monohydrate (98%) (WAKO); levoglucosan (LG) (Fluorochem); LA (98%),
113 and formic acid (FA) (98%) (Alfa Aesar); furfural (99%) and HMF ($\geq 99\%$, Sigma Aldrich); and
114 H_2SO_4 (98%, Honeywell Fluka). All standard chemicals were used as received.

115 **Catalytic conversion**

116 The catalytic conversion of bread waste substrate was performed under microwave heating
117 in a microwave reactor (Ethos Up Microwave Reactor, Milestone, maximum power of 1.9 kW)
118 following the method reported in our recent studies.^{13,20} To perform catalytic tests using a
119 monophasic system, 0.5 g bread waste (5 wt/v%), a mixture of organic solvent (PC/GVL/IPA) and
120 water (total volume 10 ml; solvent ratio 1:1 for monophasic reaction), and 0.5 M H_2SO_4 were
121 loaded in Teflon vessel and sealed, then heated to reach the desired reaction temperature (110-
122 150°C) following a constant ramp rate (32°C min⁻¹), followed by a holding stage for 1-20 min, and
123 cooling down for 20-30 min using mechanical ventilation. Each experimental run was conducted
124 in duplicates to ensure reliable analysis. The reaction conditions were selected based on the latest
125 studies on starch-rich food waste conversion^{11,13} and adjusted if necessary based on the

126 experimental observations. To substantiate the experimental results obtained in PC/H₂O solvent,
127 additional tests under the selected conditions were conducted using propylene glycol (PG) and
128 water (PG/H₂O, 1:1) for comparison.

129 After analysing the results obtained from different monophasic solvent systems, GVL/H₂O
130 and IPA/H₂O solvents were investigated for biphasic reactions. As GVL and IPA are completely
131 miscible in water, 30 wt%_(aq) NaCl was applied as a phase modifier to prepare the biphasic
132 system,^{21,25} and catalytic tests were conducted following the conditions mentioned above. It is
133 noted that the concentration of H₂SO₄ refers to the whole solvent system (i.e., consistent for all
134 experimental runs with different solvents, both monophasic and biphasic), whereas the
135 concentration of NaCl refers to the reaction phase only, which is denoted as NaCl_(aq). To analyse
136 the influence of the reaction phase and extraction phase on catalytic performance in the biphasic
137 system, different ratios of water and organic solvent (1:1, 1:3, 3:1) were applied for the conversion.
138 Control runs without bread waste substrate were performed for solvent systems under the selected
139 conditions. Standard thermocouple and pressure data-logger were used during catalytic reactions
140 to monitor and record the in-vessel reaction temperature and autogenous pressure, respectively.

141 **Analysis of samples**

142 Soluble samples were obtained from each replicate, diluted with deionised water (DIW),
143 and filtered through a membrane filter (0.45 µm) before analysis. For biphasic reactions, samples
144 were obtained from each layer and prepared separately for analysis after dilution in DIW. High-
145 performance liquid chromatography (HPLC) consisting of a Chromaster instrument equipped with
146 Aminex HPX-87H column (Bio-Rad) and a refractive index detector (Hitachi, Japan) was used to
147 analyse the soluble products; 0.01 M H₂SO₄ was used as the mobile phase at 0.5 ml min⁻¹ flow rate
148 at 50 °C.^{10,26} To ensure reliable analysis, spiked samples with known concentrations of standard

149 compounds were injected before analysing the experimental samples. The yield of products was
 150 calculated based on the carbon content (Eq. (1)) of the bread waste substrate.¹³

$$151 \quad \text{Product yield (C mol\%)} = \frac{\text{Conc}_p \text{ (mg ml}^{-1}\text{)} \times \text{Vol (ml)} / \text{MW}_p \times C_p}{C_s \text{ (mol)}} \times 100 \quad (1)$$

152 Where Conc_p denotes the concentration of products (including disaccharide, glucose, fructose, LG,
 153 HMF, LA, FA, and furfural); MW_p and C_p represent the molecular mass and number of carbons in
 154 the related product, respectively; C_s represents the total number of organic carbons in the substrate,
 155 which is 17.3 mmol for 0.5 g of bread waste. A volume loss of 5-15% (following various reaction
 156 duration) was recorded for PC/H₂O solvent, which was taken into account for calculating the
 157 soluble product yields. For biphasic systems, partition coefficients (R_x) for a particular product
 158 such as LA (R_{LA}) and FA (R_{FA}) were calculated following Eq. (2),

$$159 \quad \text{Partition coefficient (} R_x \text{)} = \frac{\text{C mol\% of product in the organic layer}}{\text{C mol\% of product in the aqueous layer}} \quad (2)$$

160 Post-reaction solid residues were collected through centrifugation and decantation; washed
 161 with DIW three times and oven-dried for 48 h at 60°C and then ground as a powder for further
 162 analysis using ¹³C nuclear magnetic resonance (NMR). Solid ¹³C NMR were recorded with bulk
 163 powder samples on a Jeol JNM-ECZ500R MHz spectrometer operating at a resonance frequency
 164 of 125 MHz. A commercial 3.2 mm magic-angle spinning (MAS) NMR probe was used with a
 165 standard cross-polarisation MAS (CPMAS) pulse sequence. The MAS frequency was 10 kHz with
 166 relaxation delay, scan times, and contact time at 5 s, 1200-2000, and 2 ms, respectively. Liquid
 167 samples subjected to the selected reaction conditions were also analysed by ¹³C NMR using D₂O
 168 solution. Chemical shifts (δ) were given in ppm and measured relative to tetramethylsilane (TMS)
 169 as the internal standard. The solid residues were also characterised by X-ray diffraction (XRD)

170 (Rigaku Smatlab, 5° to 50° 2θ , rate: $10^\circ \text{ min}^{-1}$ at 45 kV and 200 mA) and the crystallinity index
171 (*CrI*) was calculated from XRD patterns following the method reported in the literature.²⁷

172 **Results and discussion**

173 **Catalytic conversion of bread waste under bio-derived and CO₂-derived solvents**

174 Facile conversion of bread waste was achieved under moderate reaction conditions,
175 obtaining 45-72 mol% total product yield at 130°C under bio-derived and CO₂-derived co-solvent
176 systems (**Fig. 1a**). For H₂O, PC/H₂O, and GVL/H₂O solvents, the maximum total sugars released
177 from bread waste were 64-70 mol% in a short reaction duration of 1 min (**Fig. S1a**). In contrast,
178 using IPA/H₂O, the total sugar yield after 1 min of reaction was 43.5 mol%, increasing up to 48.8
179 mol% when the reaction was prolonged for 20 min. Given the total sugar yield generated at 110°C
180 (**Fig. 1b**), hydrolysis of bread waste was faster in GVL/H₂O (48.1 mol%) and PC/H₂O (53.7 mol%)
181 compared to H₂O (~30 mol%) and IPA/H₂O (9.4 mol%). With increasing reaction duration up to
182 20 min, sugar yield in H₂O and IPA/H₂O remained steady and generated an insignificant LA yield
183 ~1.5 mol% after 20 min of reaction. In contrast, sugars were consumed, and LA yield increased
184 with increasing reaction duration gradually in GVL/H₂O (up to 4.8 mol%) and sharply in PC/H₂O
185 (up to 19.6 mol%) (**Fig. 1a**). ¹³C NMR spectra of reacted solutions (1 and 20 min reaction) (**Fig.**
186 **2a**) provided further evidence for the disparity in catalytic conversion under different solvent
187 systems. ¹³C NMR chemical shift (δ) at 95.8 ppm, attributed to glucose,²⁸ was observed for all
188 reactions. The highest intensity of glucose peak was observed for 1 min reacted solution in
189 PC/H₂O, which agrees with the maximum sugar yield measured by HPLC. In contrast, the lowest
190 intensity of glucose peak and emerged LA peak (at 27.7, 37.6, 177 pm) along with an FA peak (at
191 165.45 ppm)²⁹ for 20 min reaction in PC/H₂O further prove the efficient tandem catalysis in
192 PC/H₂O. The characteristic peaks for LA and FA were not detectable in IPA/H₂O and H₂O, while

193 low-intensity peaks could be observed for GVL/H₂O. Besides, representative solvent peaks²⁹ were
194 detected in the reacted solutions indicated in **Fig. 2a**.

195 The higher soluble product yields in PC/H₂O and GVL/H₂O (**Fig. 1b**) could be related to
196 the high reactivity of the Brønsted acid catalyst due to the availability of highly active proton in
197 the presence of aprotic co-solvents in the reaction system.^{13,30} The extent of proton stabilisation
198 influences the acid dissociation constant, and in water lowers the proton reactivity, which
199 subsequently elevates the required energy level for acid-catalysed biomass conversion reactions
200 such as hydrolysis and dehydration.³⁰ Therefore, reaction kinetics could be slower in H₂O (100%)
201 compared to a solvent system consisting of a polar aprotic solvent such as GVL and PC, which
202 might enhance the reaction rates owing to reactive proton and facile glycosidic bond cleavage.^{20,31}
203 For instance, a recent study reported a ten-fold increase in reaction rate for acid-catalysed
204 conversion of HMF to LA using GVL with 10% H₂O compared to 100% H₂O as solvent.³² Slower
205 conversion of bread waste was observable in the case of IPA/H₂O solvent (total sugar ~10 mol%,
206 at 110°C, 1 min) (**Fig. 1b**), where both co-solvents are protic and probably hamper the proton
207 reactivity during conversion.

208 The starch contained in the bread waste substrate represents a complex structure combining
209 linear amylose chains and highly branched amylopectin comprising $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$
210 glycosidic bonds. ¹³C NMR spectra of solid residues (**Fig. 2b**) subjected to reaction under different
211 solvent systems (20 min) showed differences in chemical shifts than the untreated bread waste,
212 possibly related to the changes in starch structures.³³ The chemical shifts observed at resonance
213 values of 93-103, 74-85, 64-73, 55-60 ppm can be attributed to C1, C4, C2,3,5, and C6 of glucose
214 units, respectively.^{11,34} Resonance values attributed to C1 and C4 can be helpful to understand the
215 changes in the amorphous and highly ordered/crystalline state of starch. The C1 resonance for

216 post-reaction solid residues shifted toward 98-103 ppm, presenting comparatively sharp peaks
217 compared to the broad peak observed at 93-100 ppm for untreated bread waste. The broad shoulder
218 observed around 95 ppm for untreated bread waste is characteristic of the amorphous domain of
219 C1. In contrast, a sharp peak observed around 100 ppm (C1) for solid residues might indicate a
220 decrease in amorphous content and a subsequent rise in relative crystallinity, which was previously
221 reported for acid-modified starch.³⁴⁻³⁵ In contrast, the resonance for C4 around 82 ppm was
222 observed for solid residues, characteristic of an amorphous state.³⁶ Different changes in chemical
223 shifts in different carbon regions can reflect varied transformations between amylose and
224 amylopectin within the starch structures. Amylose is mainly amorphous and more susceptible to
225 acid hydrolysis than amylopectin, which comprises highly ordered/crystalline domain building
226 double-helical structures. However, initially during acid hydrolysis, amorphous amylose could be
227 partially transformed into double helices resistant to acid hydrolysis, and consequently, crystalline
228 content could be enhanced relative to amorphous content.³⁷⁻³⁸ The observed changes in solid
229 residues compared to untreated bread waste was substantiated by XRD analysis. The XRD pattern
230 of untreated bread waste (**Fig. S2**) showed a broad crystalline peak at $\sim 2\theta=20^\circ$, and the calculated
231 *CrI* value was ~ 0.51 , whereas solid residues in different solvent systems provided *CrI* values
232 ranging $\sim 0.73-0.78$. This also suggested the rapid decomposition of amorphous region of starch
233 granules during acid hydrolysis resulting in an increased relative crystallinity.²⁷

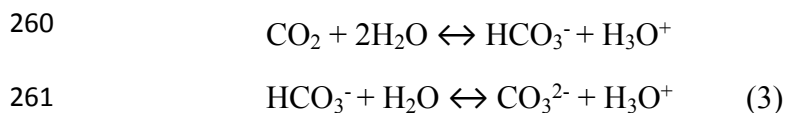
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235 LA yield enhanced by in-vessel high pressure generated in PC/H₂O

236 Comparing different co-solvent systems, PC/H₂O was found to be the best for LA
237 production, generating 19.6 mol% after 20 min reaction at 130°C (**Fig. 1a**), which is promising
238 considering mild reaction conditions used in this study and the reported literature results under
239 comparable experimental conditions.^{9,39} Under GVL/H₂O solvent, sugars depleted gradually
240 during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H₂O solvent, sugars
241 started to deplete rapidly during 3-20 min of reaction, and 19.6 mol% LA yield was achieved after
242 20 min. A significant in-vessel pressure build-up was recorded during reaction in PC/H₂O,
243 reaching a maximum ~27 bar at 130°C, 20 min compared to reactions in other solvents (**Fig. 3a**).
244 Compared to the autogenous in-vessel pressure (~13 bar) generated in PC/H₂O during 1 min
245 reaction, the reaction pressure level almost doubled (~23-27 bar) during 3-20 min reaction (**Fig.**
246 **3b**), which was analogous to rapid sugar consumption and a sharp increase in LA yield (4-19.6
247 mol%) during 3-20 min. In acidic conditions, PC solvent could decompose into PG and CO₂ as
248 reported in the literature.^{13,40} Noticeably, ~5-15% solvent loss was recorded for reactions in
249 PC/H₂O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the
250 reaction. Besides, ¹³C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H₂O (1 and 20
251 min) showed peaks at 66.4 and 67.7 ppm representing PG.²⁹ The PG peaks had comparatively
252 higher intensity after 20 min reaction than 1 min, suggesting that a higher fraction of PC was
253 decomposed to PG, which was consistent with higher CO₂ pressure recorded for more prolonged
254 reactions in PC/H₂O (**Fig. 3b**).

255 Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from
256 CO₂ generation during catalytic conversion in PC/H₂O might enhance the LA production rate.
257 Another influential factor could be the increased acidity due to carbonic acid derived from partial

258 dissolution of CO₂ during the reaction, which might enhance sugar dehydration.⁴¹ Solution acidity
259 can arise through *in situ* formation and dissociation of carbonic acid, as given in Eq. (3).⁴²



262 The acidity (pH) associated with CO₂ generated during 3-20 min reaction in PC/H₂O was
263 estimated, following the scheme reported in the literature.⁴³⁻⁴⁴ The estimated CO₂-derived pH
264 value for specified reaction conditions was ~3.5, i.e., considerably higher than the H₂SO₄ derived
265 pH (~0.5) in this study. Therefore, CO₂-derived pH on its own might not be sufficient to catalyse
266 tandem reactions and significantly enhance LA yield. In other words, LA yield might be improved
267 probably by PC/H₂O generated CO₂ pressure more than CO₂-derived acidity during the catalytic
268 conversion of bread waste. To testify this postulation, an additional test using PC/H₂O was
269 conducted, in which autogenous pressure developed due to PC degradation (~22 bar) was released
270 after 5 min reaction, and then the solution underwent reaction for another 15 min (**Fig. 3c**).
271 Compared to continuous 20 min reaction in PC/H₂O (LA yield 19.6 mol%), only about half of LA
272 was produced (LA yield 11.2 mol%) when the pressure was released prematurely during the
273 reaction. After the pressure release, the autogenous pressure was ~4.2 bar from the beginning till
274 the end point of additional 15-min reaction. Moreover, supplementary tests using PG/H₂O only
275 generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA
276 yield obtained in PC/H₂O, therefore disproving any favourable influences by PG solvent
277 (decomposed from PC) on the catalytic performance. These experimental evidences confirm the
278 crucial enhancement of reaction pressure on the catalytic LA production.

279 Intensification of LA yield through phase separation

280 Among co-solvent systems, PC/H₂O generated the highest LA yield 19.6 mol% at 130°C, and
281 ~9 mol% soluble sugar remained after a 20 min reaction. In contrast, ~47-49 mol% soluble sugar
282 was available after 20 min reaction in GVL/H₂O and IPA/H₂O (**Fig. 1a**), which could be further
283 converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H₂O
284 and IPA/H₂O, conversion of bread waste was conducted at 150°C for 1-20 min reaction duration
285 (**Fig. 4a&b**). As higher temperature provided more energy for the reaction, LA yield increased
286 gradually up to 16.4 mol% in GVL/H₂O (150°C, 20 min) (**Fig. 4b**), which was more than three
287 times higher than the maximum LA yield achieved at 130°C (4.8 mol%, 20 min). The maximum
288 LA yield achieved in IPA/H₂O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than
289 GVL/H₂O system, corroborating the positive role of aprotic GVL solvent in enhancing proton
290 reactivity for less energy-intensive tandem catalysis.^{10,30}

291 The biphasic solvent systems (prepared using 30 wt% NaCl_(aq)) were further investigated
292 as an intensification scheme to improve the concentration of the target product LA in this study.
293 Promisingly, the concentration of LA at the end of the reaction (150°C, 20 min) increased ~1.6
294 times in both biphasic GVL/H₂O and IPA/H₂O systems (**Fig. 4c**) compared to analogous
295 monophasic systems. Though total soluble product yields were comparable in the two biphasic
296 systems (~33-35 mol%) (**Fig. S1b**), the distributions of soluble products were distinctive between
297 GVL/H₂O and IPA/H₂O. While biphasic GVL/H₂O selectively generated LA as the main product
298 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H₂O biphasic contained 10.6 mol% LA, 2.6
299 mol% FA, ~7 mol% HMF, and 10.2 mol% remaining sugars (glucose and fructose) (**Fig. 4c**). A
300 considerable fraction of HMF present in both monophasic and biphasic IPA/H₂O indicated that
301 the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely

302 recommended solvent for HMF production, IPA can create a shielding effect around HMF that
303 helps to prevent its rehydration and suppress further conversion to byproducts such as insoluble
304 humins.⁴⁵⁻⁴⁶ A recent study revealed that the rate constant for fructose to HMF was considerably
305 higher than that of HMF to degradation products when IPA was present in the solvent system,⁴⁶
306 echoing the experimental observations in this study where low LA selectivity was obtained in
307 IPA/H₂O solvent system. In other words, IPA/H₂O could be considered as a potential solvent for
308 HMF production in future investigations. By contrast, in the presence of GVL solvent, H₂SO₄
309 catalysed HMF production could be rapid and readily converted to LA at high acid strength.⁴⁷
310 Considerable LA yield achieved in biphasic GVL/H₂O in this study (26.8 mol%, at 150°C, 20 min)
311 proves the high efficiency of H₂SO₄/GVL/H₂O system for LA production.

312 As GVL/H₂O biphasic solvent was the most efficient for intensifying LA yield at moderate
313 conditions, a comprehensive investigation was conducted for bread waste conversion in the co-
314 solvent system following varied reaction conditions (150°C, 10-20 min). In biphasic GVL/H₂O,
315 LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H₂O,
316 1:1) (**Fig. 5a**). However, a slight decrease in LA yield was observed after 20 min, suggesting that
317 LA started to degrade with prolonged reaction. The major product in monophasic GVL/H₂O (1:1,
318 15 min) was glucose (34.6 mol%), while the biphasic system selectively generated LA (~28 mol%)
319 as the major product. The LA yield increased up to ~2.5 times in the biphasic system compared to
320 the monophasic one (~11 mol%) (150°C, 15 min), implying that phase separation could be
321 beneficial for intensive LA production and upscaling to industrial scale.

322 Essentially, to develop an efficient biphasic reaction medium, it is necessary to understand
323 the contribution and influences of the reaction phase (H₂O) and the extraction phase (GVL) to
324 optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H₂O

325 biphasic system, catalytic tests were conducted with various ratios of GVL and H₂O (1:1, 1:3, and
326 3:1 of GVL/H₂O). The partition coefficient for LA (R_{LA}) in the GVL/H₂O biphasic solvent was
327 calculated to evaluate the effect of the extraction phase (GVL) in the system. The R_{LA} achieved for
328 10-15 min reaction was 4.2 when 1:1 GVL/H₂O was applied for reaction (**Fig. 5b**), indicating a
329 higher distribution of LA in the organic phase compared to the aqueous phase. Therefore, GVL
330 solvent can be considered highly effective for reactive LA extraction. The partitioning of LA
331 obtained in this study (R_{LA} 4.2) is comparable to a previous study that reported R_{LA} ranging 3.7-4
332 using cellulose as feedstock.²¹

333 The total yield of LA increased (27.4-32 mol%) when a higher fraction of H₂O (1:3,
334 GVL/H₂O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-
335 17.1 mol%) when a lower fraction of H₂O (3:1, GVL/H₂O) was applied (**Fig. 5b**). Though the total
336 LA yield increased with a higher fraction of H₂O, the extraction of LA was found to be inefficient.
337 The partition coefficient achieved was only 1.1 (1:3, GVL/H₂O), indicating nearly even
338 distribution of produced LA in the reaction and extraction phases due to the lower fraction of GVL
339 applied. In comparison, ~97% of the total LA produced was extracted into the GVL phase when a
340 higher fraction of GVL (3:1, GVL/H₂O) was applied for reaction. However, a considerable
341 decrease in total LA yield was observed, possibly due to the lack of sufficient aqueous phase
342 available for reaction. These observations suggested the indispensable contribution of both
343 reaction and extraction phases for an efficient biphasic system for LA production. Considering LA
344 yield (27.4 mol%) and R_{LA} (4.2), the 1:1 GVL/H₂O biphasic system (150°C, 15 min) provided the
345 best performance for intensive LA production.

346 To reflect further on the mechanism and roles of catalytic species in NaCl modified
347 GVL/H₂O biphasic system, additional tests were performed under the selected reaction conditions.

348 In the case of reaction conducted with only NaCl (30 wt%) without acid catalyst, only marginal
349 product yield was observed (**Fig. 6a**). When NaCl was applied together with H₂SO₄ for bread
350 waste conversion, an increase in LA yield was observed compared to the reaction in the presence
351 of H₂SO₄ without salt addition. These observations indicate that NaCl alone could not catalyse the
352 desired reaction yet it may act synergistically with H₂SO₄ enhancing the LA production in the
353 aqueous phase during biphasic conversion of bread waste. Product distributions in the aqueous and
354 GVL phases in the specified reaction conditions are provided in **Fig. S3**. The synergistic catalysis
355 by NaCl and H₂SO₄ together with simultaneous efficient extraction of LA into GVL could account
356 for the high LA yield obtained in the GVL/H₂O biphasic system.

357 Moreover, the recyclability of the aqueous phase containing H₂SO₄ was investigated. After
358 the catalytic run (reaction and cooling), the reacted organic phase was removed and fresh GVL
359 and bread waste substrate were applied for another cycle of catalytic reaction (run-2) again while
360 retaining the aqueous phase from the previous run without adding extra H₂SO₄. Similarly, the third
361 cycle of catalytic reaction (run-3) was conducted. In the 2nd and 3rd run (**Fig. 6b**), 15 mol% and 13
362 mol% LA was obtained, respectively, compared to the LA yield (28 mol%) obtained in the initial
363 run, which suggested that the acid catalyst could be retained in the aqueous phase and recycled for
364 further conversion, though a certain degree of decrease in LA yield was observed. Future studies
365 would be required for evaluating the biphasic system in a continuous reaction mode, which may
366 be more efficient compared to the batch reaction mode.

367 Apart from LA as the target product, FA yield was analysed for bread waste conversion in
368 monophasic and biphasic GVL/H₂O, as FA is often co-produced during biomass conversion.⁴⁸
369 Similar to LA, the FA yield was enhanced through phase separation with the yield from ~2-3 mol%
370 in the monophasic system to a maximum 5.4 mol% FA yield in biphasic GVL/H₂O (150°C, 15

371 min, 1:3 solvent ratio) (**Fig. 5c**). Using 1:1 GVL/H₂O, FA partition coefficient (R_{FA}) obtained was
372 ~2-3 (150°C, 10-20 min, solvent ratio 1:1) (**Fig. 5c**), indicating that FA could also be
373 simultaneously extracted into the GVL layer during bread waste conversion. Besides, partition
374 coefficients for LA, FA, and HMF were evaluated in IPA/H₂O solvent (150°C, 20 min, 1:1 solvent
375 ratio), and the values were 6.6, 5.4, and 5.7, respectively (**Fig. S4**), corroborating an effective
376 extraction of these compounds into the organic phase. Considering the low LA selectivity and total
377 LA yield (10.6 mol% at 150°C, 20 min), further investigation was discontinued for IPA/H₂O.

378 **Perspectives on LA production and solvent recycling**

379 To evaluate the efficiency of the catalytic system for LA production, LA yield relative to
380 theoretical LA yield of bread waste substrate (considering total available carbohydrate and
381 possible maximum theoretical yield (64.5%)) was calculated and compared with the reported
382 achievements with commercially available starch substrates in the existing literature (**Table 1**).
383 For PC/H₂O (130°C, 20 min) and GVL/H₂O biphasic solvents (150°C, 15 min), 45.7% and 66%
384 LA yield was achieved relative to theoretical yield, respectively. This is considered promising in
385 comparison to the reported LA yield (45.6-66.4%) from commercially available starch substrates
386 in previous studies⁴⁹⁻⁵⁰ where the conversion was conducted using comparatively harsh reaction
387 conditions. For other recent studies where no direct comparison is possible due to the lack of data
388 regarding relative LA yield,^{17,51} it should be noted that much longer reaction duration was required
389 to obtain the reported LA yield.

390 The recyclability of GVL/H₂O biphasic solvent was investigated and discussed in the
391 previous section. For PC/H₂O solvent, despite partial decomposition of PC during acid catalysis,
392 it offers various advantages as a solvent because a high product yield can be obtained with a
393 moderate temperature and a short duration, which play a critical role in reducing the energy

394 consumption and reactor size. The production of PC from CO₂ is beneficial for process economy
395 and environmental sustainability in terms of CO₂ utilisation. In the application of PC solvent, the
396 derived CO₂ after reaction can be captured and recycled for PC production or other CO₂ based
397 biorefineries, which are conducive to fostering the circular economy. The spent organic solvents
398 can be recycled after separation and purification following commonly used techniques such as
399 fractional distillation. For instance, a comprehensive life cycle assessment (LCA) on solvent waste
400 recovery⁵² demonstrated that implementing a solvent recovery system can reduce the
401 environmental footprint of the total solvent manufacturing, usage, and disposal process. The
402 energy requirements and emissions associated with the solvent recovery process have been
403 recognised to be trivial in comparison to the emissions due to virgin solvent production and spent
404 solvent disposal by incineration.

405 **Conclusions**

406 This study provides comprehensive insights into the critical factors for intensive LA
407 production, which can be conducive to the technology scale-up. The bio-derived and CO₂-derived
408 co-solvents in this study, i.e., PC/H₂O, GVL/H₂O, IPA/H₂O, could facilitate H₂SO₄ catalysed
409 tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency.
410 PC/H₂O solvent was the most efficient for LA production using moderate reaction conditions,
411 which could be attributed to the CO₂ pressure generated *in situ* through solvent (PC) degradation.
412 Besides, catalytic performance could be significantly enhanced in GVL/H₂O and IPA/H₂O using
413 the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the
414 final concentration of LA. GVL/H₂O biphasic solvent seems promising considering LA yield (28
415 mol%) and LA partitioning (R_{LA} 4.2) achieved in the study. The bio-derived and CO₂-derived

416 solvents applied in this study can be considered as emerging solvents and potential alternatives to
417 common industrial solvents in future biorefinery applications.

418

419 **Supplementary information**

420 The supplementary information is available online.

421

422 **Conflicts of interest**

423 The authors declare no conflict of interest.

424

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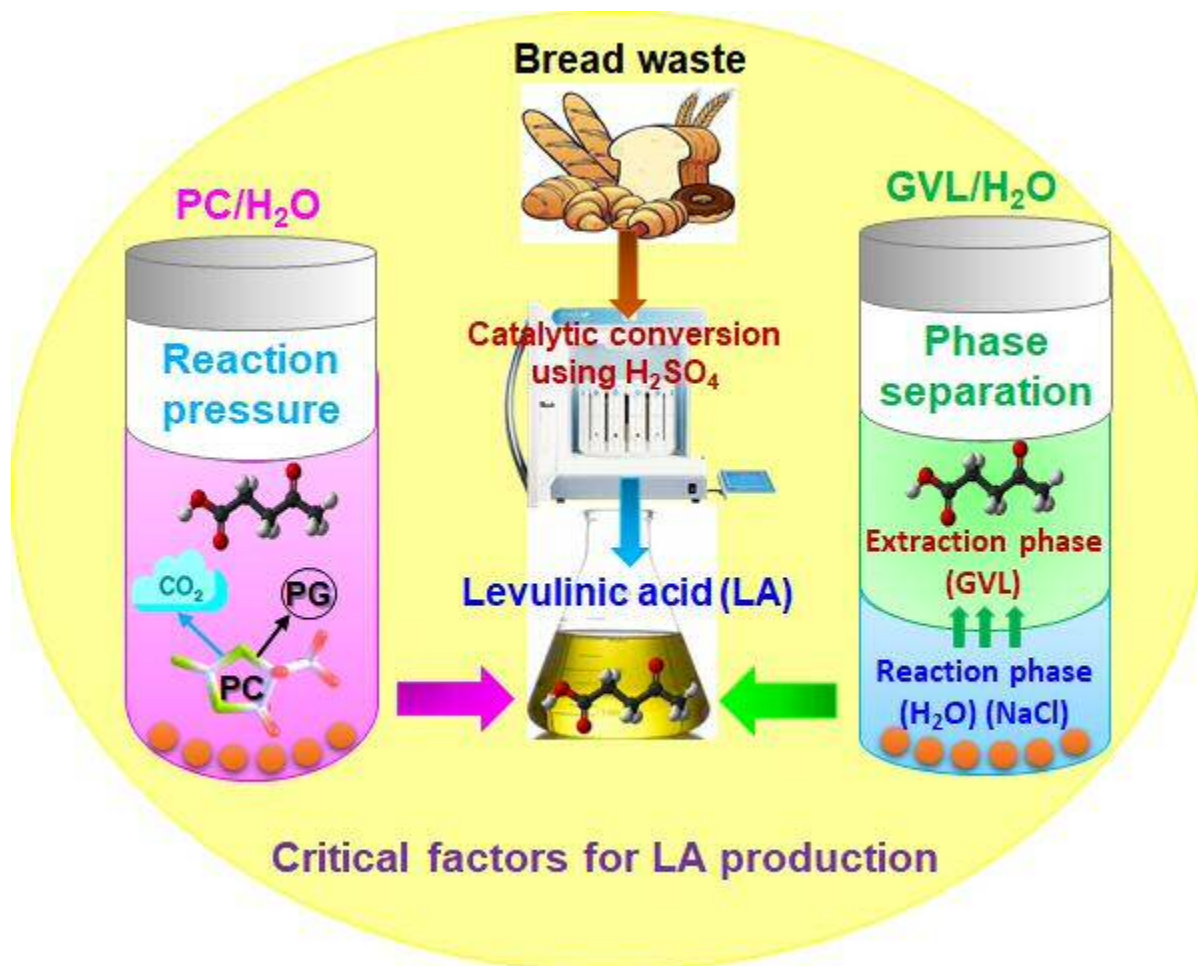
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Table of Content



Synopsis:

This study provides new and critical insights into sustainable catalytic conversion of food (bread) waste to platform chemicals for achieving sustainable development goals and fostering a circular economy.

Critical factors for levulinic acid production from starch-rich food waste:

Solvent effects, reaction pressure and phase separation

List of figures:

- Fig. 1.** Total sugar yield and LA yield during the catalytic conversion of bread waste in different solvents (a) at 130°C, 1-20 min, (b) at 110°C, 1 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 1:1 solvent ratio).
- Fig. 2.** (a) ¹³C NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 1 min & 20 min, 1:1 solvent ratio), (b) ¹³C solid-state NMR spectra of untreated bread waste and solid residues collected after reaction under different solvent systems (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 20 min, 1:1 solvent ratio).
- Fig. 3.** (a) Pressure profile during the catalytic conversion of bread waste in different solvents for 20 min reaction, (b) pressure profile in PC/H₂O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H₂O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H₂O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 1:1 solvent ratio).
- Fig. 4.** Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H₂O (monophasic) and (b) GVL/H₂O (monophasic); (c) comparative product yields in IPA/H₂O and GVL/H₂O monophasic and biphasic medium (30 wt% NaCl_(aq)) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 1:1 solvent ratio).
- Fig. 5.** (a) Product yields during the catalytic conversion of bread waste in GVL/H₂O monophasic and biphasic medium comprising different solvent ratios; (b) LA and (c) FA distribution in the organic and aqueous phase and partition coefficients obtained for the catalytic conversion of bread waste in GVL/H₂O biphasic medium comprising different solvent ratios (Note: values for partition coefficient are not shown for solvent ratio 3:1 as ~97% of the total LA and ~92% of the total FA produced were extracted to the organic phase) (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 10-20 min).
- Fig. 6.** (a) LA yield and total product yield under different reaction conditions (Reaction conditions: 5 wt% substrate loading, 150°C), (b) LA yield and other product yields (sugar+HMF+furfural) in consecutive runs in GVL/H₂O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 15 min, solvent ratio 1:1).

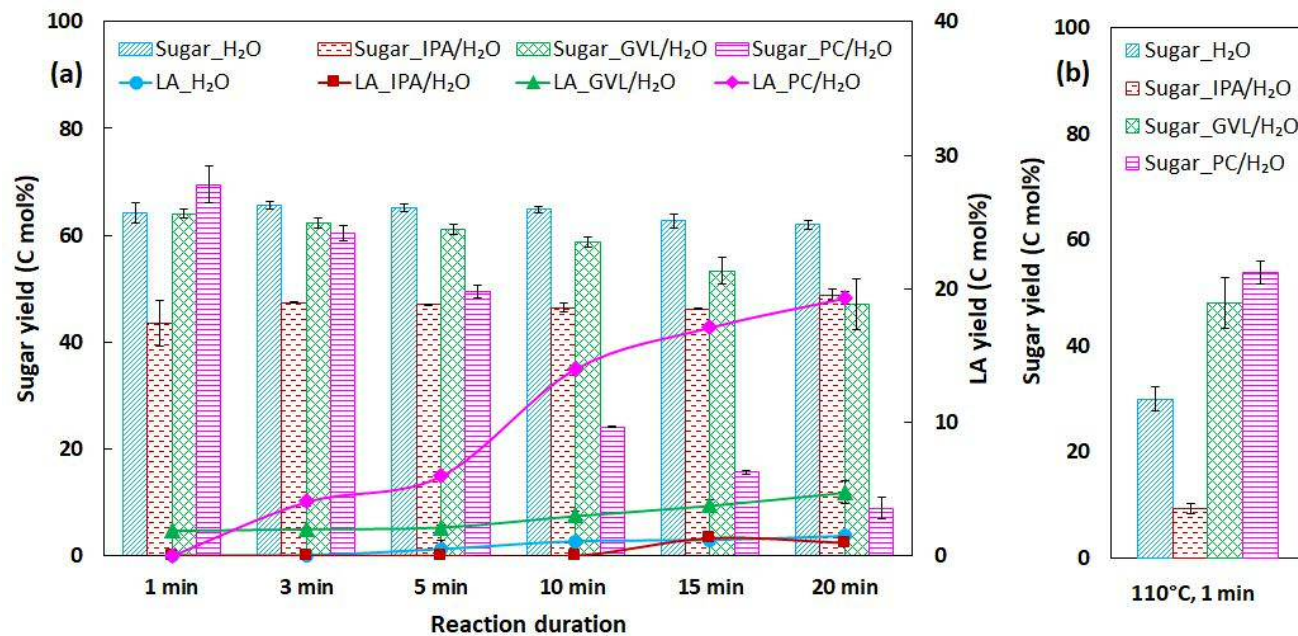


Fig. 1. Total sugar yield and LA yield during the catalytic conversion of bread waste in different solvents (a) at 130°C, 1-20 min, (b) at 110°C, 1 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 1:1 solvent ratio).

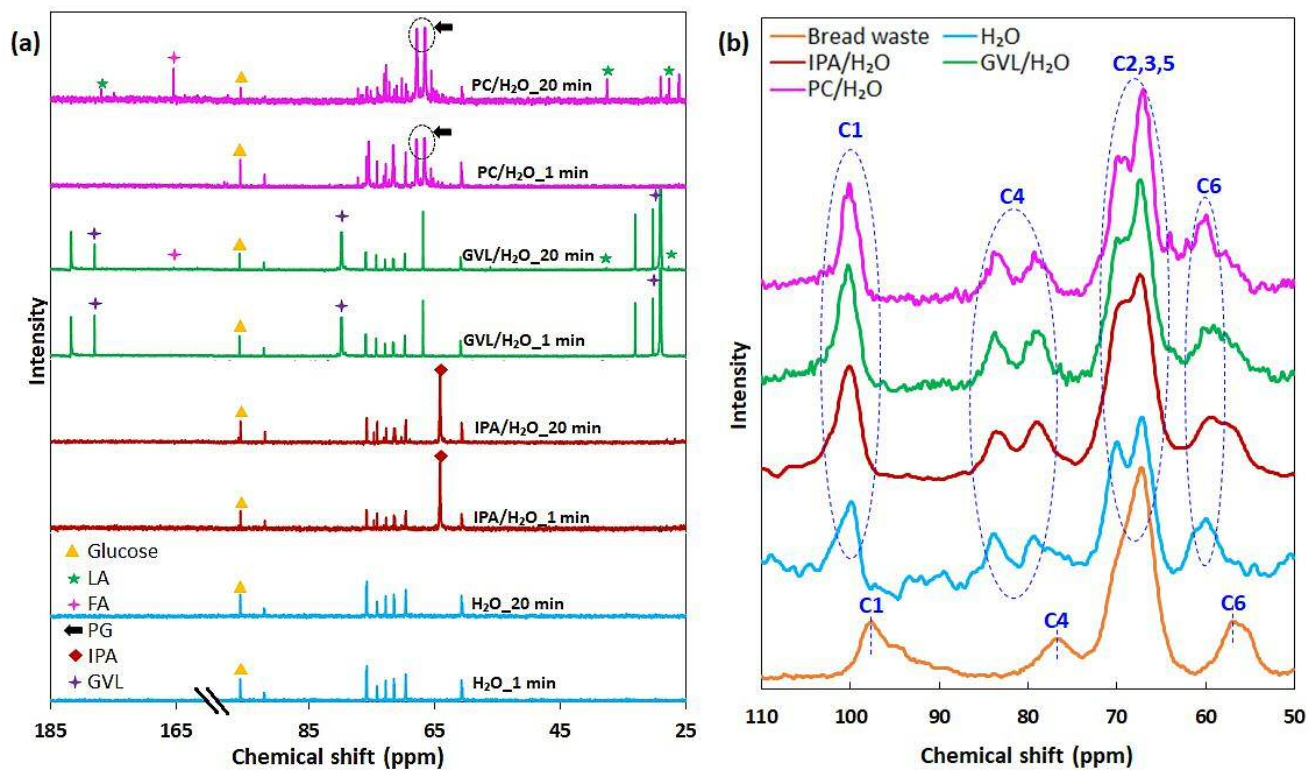


Fig. 2. (a) ^{13}C NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M H_2SO_4 , 130°C, 1 min & 20 min, 1:1 solvent ratio), (b) ^{13}C solid-state NMR spectra of untreated bread waste and solid residues collected after reaction under different solvent systems (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4 , 130°C, 20 min, 1:1 solvent ratio).

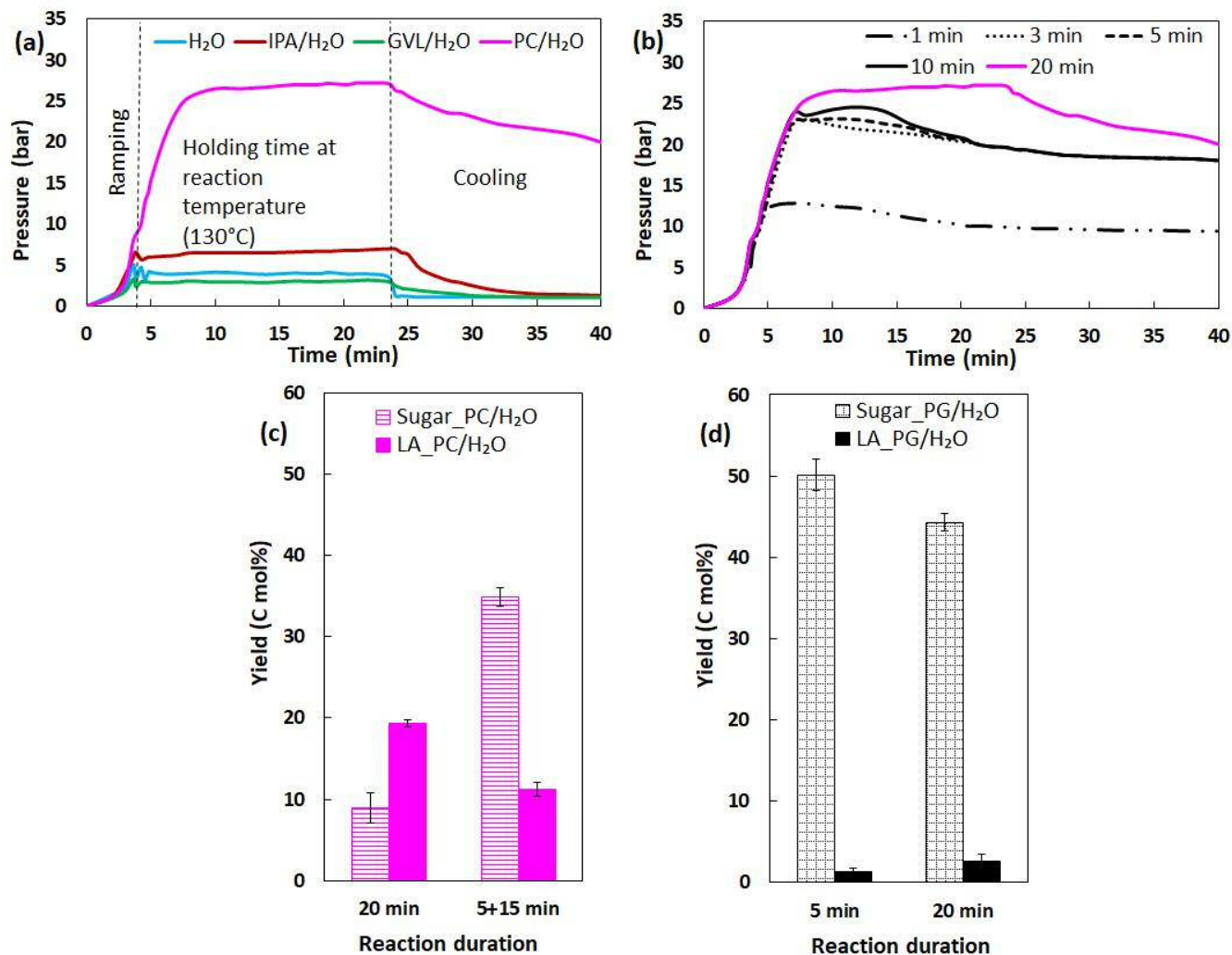


Fig. 3. (a) Pressure profile during the catalytic conversion of bread waste in different solvents for 20 min reaction, (b) pressure profile in PC/H₂O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H₂O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H₂O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 1:1 solvent ratio).

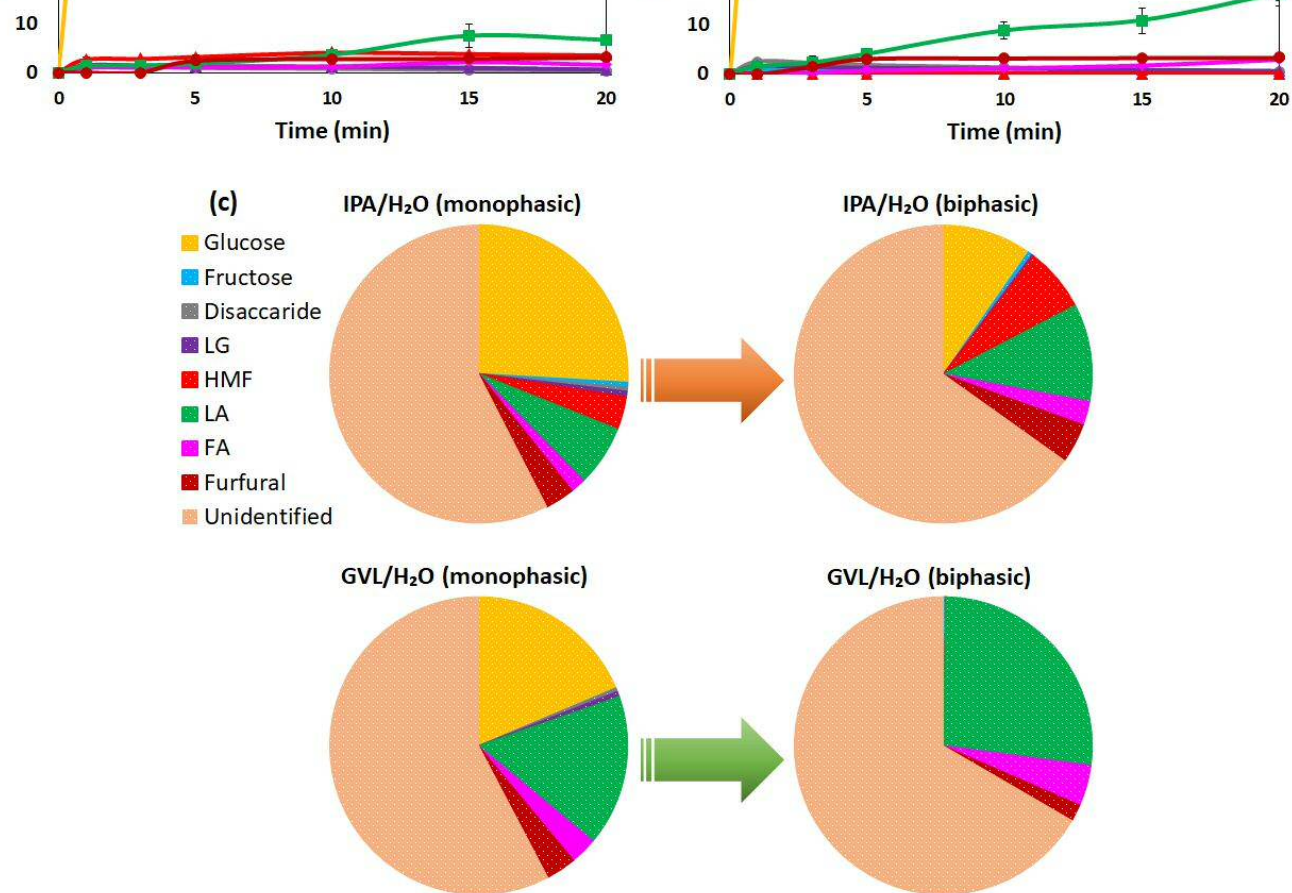


Fig. 4. Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H₂O (monophasic) and (b) GVL/H₂O (monophasic); (c) comparative product yields in IPA/H₂O and GVL/H₂O monophasic and biphasic medium (30 wt% NaCl_(aq)) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 1:1 solvent ratio).

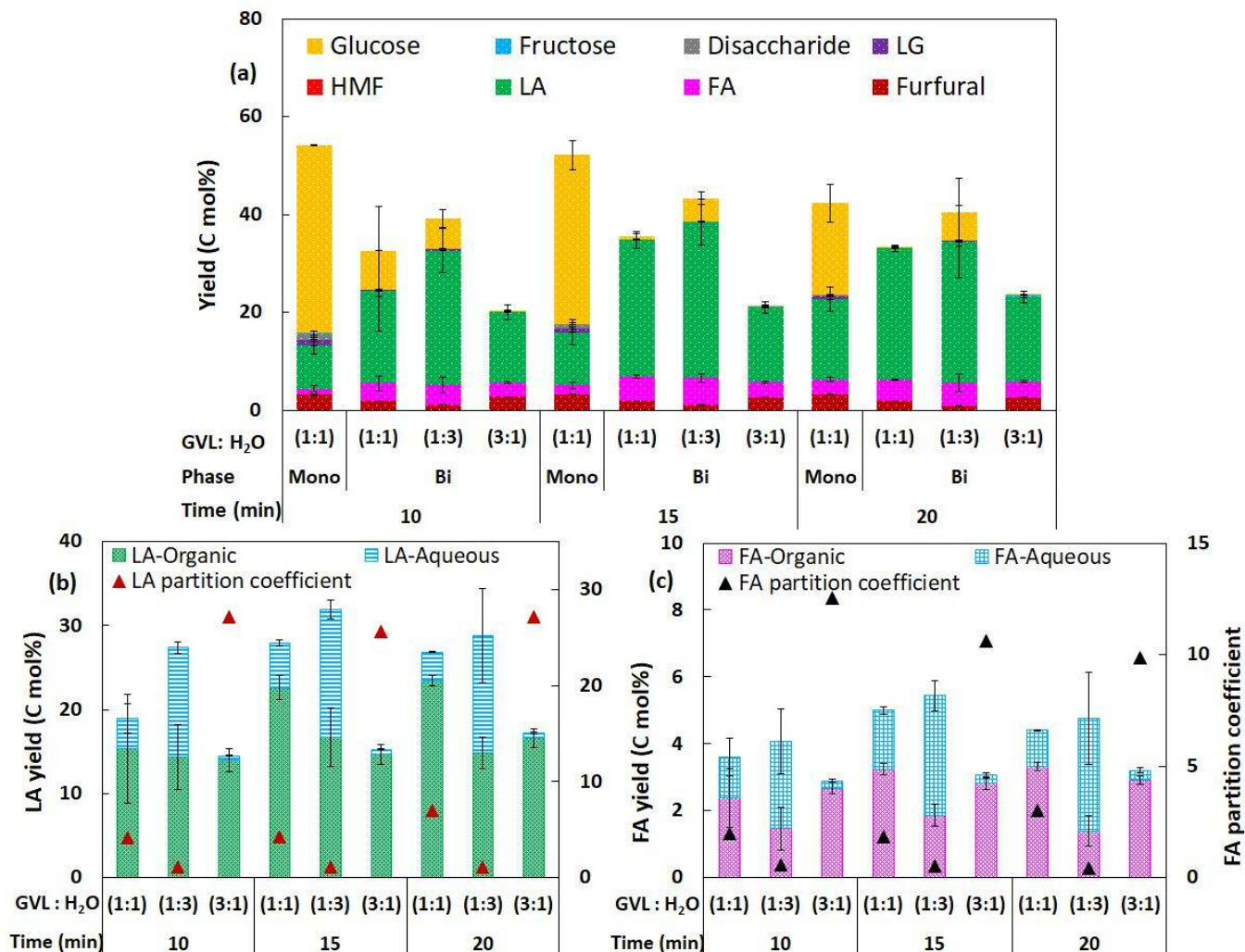


Fig. 5. (a) Product yields during the catalytic conversion of bread waste in GVL/H₂O monophasic and biphasic medium comprising different solvent ratios; (b) LA and (c) FA distribution in the organic and aqueous phase and partition coefficients obtained for the catalytic conversion of bread waste in GVL/H₂O biphasic medium comprising different solvent ratio (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 10-20 min).

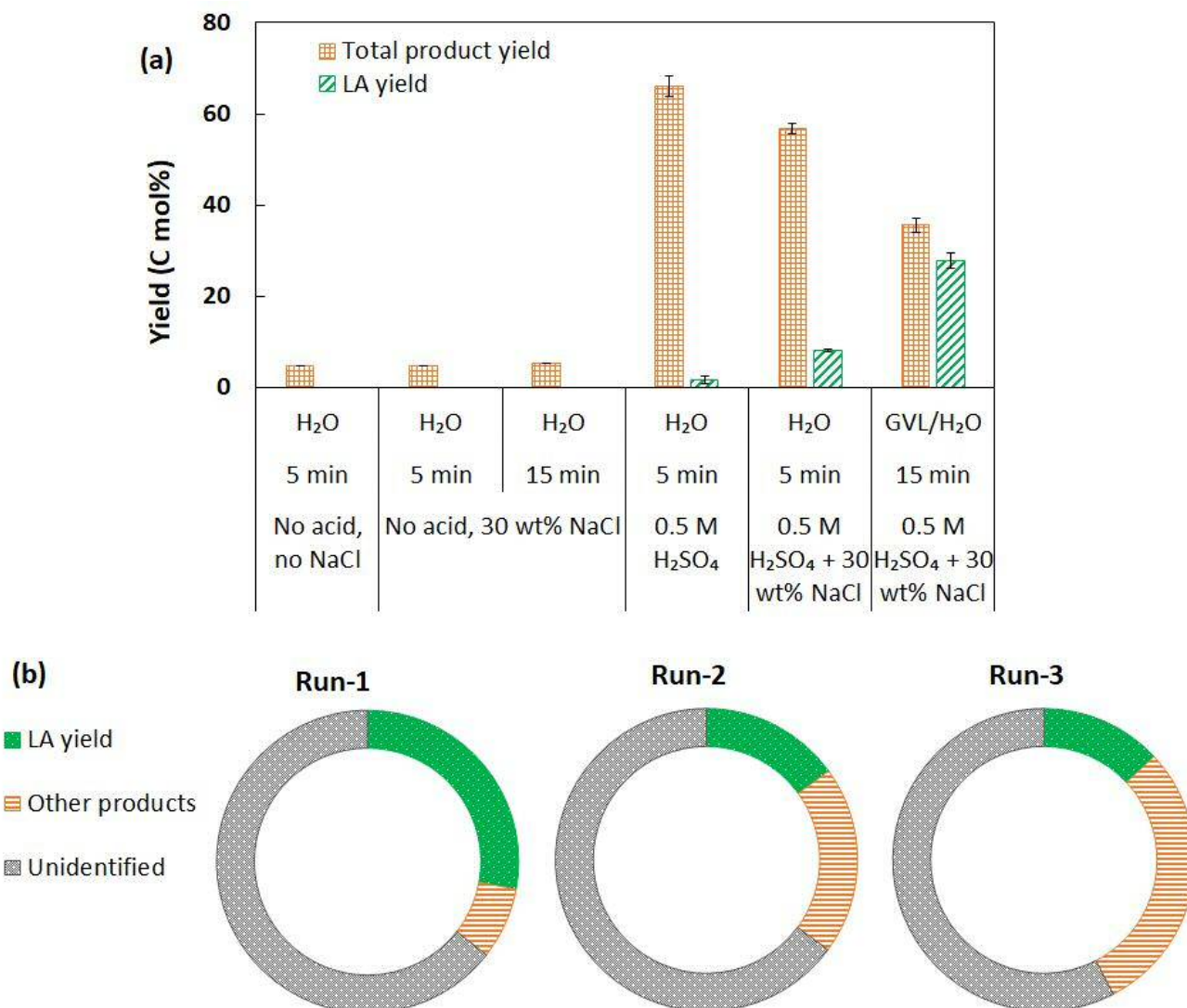


Fig. 6. (a) LA yield and total product yield under different reaction conditions (Reaction conditions: 5 wt% substrate loading, 150°C), (b) LA yield and other products (sugar+HMF+furfural) of consecutive runs in GVL/H₂O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 15 min, solvent ratio 1:1).

Table 1. Comparative LA yield obtained from bread waste in this study and from starch substrates in the literature

Substrate	Reaction conditions	Catalyst	LA yield based on total organic carbon (mol%)	LA yield based on weight of substrate (%)	LA yield to the yield
Bread waste	130°C, 20 min, H ₂ O	0.5 M H ₂ SO ₄	1.5	1.2	1
	130°C, 20 min, IPA/H ₂ O		1.0	0.8	1
	130°C, 20 min, GVL/H ₂ O		4.8	3.8	1
	130°C, 20 min, PC/H ₂ O		19.6	15.5	4
	150°C, 20 min, IPA/H ₂ O (mono)		6.6	5.3	1
	150°C, 20 min, IPA/H ₂ O (bi)		10.6	8.5	2
	150°C, 15 min, GVL/H ₂ O (mono)		10.9	8.8	2
	150°C, 15 min, GVL/H ₂ O (bi)		27.9	22.4	6
	150°C, 20 min, GVL/H ₂ O (mono)		16.4	13.2	3
	150°C, 20 min, GVL/H ₂ O (bi)		26.8	21.6	6
Bread	130°C, 8 h	1.5 ml 5 M H ₂ SO ₄ and 10 ml GVL	-	30.2	
Starch	165°C, 5 h	sulfonated hyperbranched poly(arylene oxindole)s	-	31.1	
Starch	200°C, 60 min	4% H ₂ SO ₄	-	47.5	6
Sorghum grain	200°C, 40 min	8% H ₂ SO ₄		32.6	4

Supplementary Information

Critical factors for levulinic acid production from starch-rich food waste: Solvent effects, reaction pressure and phase separation

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- Fig. S1.** Total product yields during the catalytic conversion of bread waste under different solvents at (a) at 130°C and (b) at 130°C and 150°C under GVL/H₂O and IPA/H₂O (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 1-20 min, 1:1 solvent ratio).
- Fig. S2.** XRD pattern of untreated bread waste and solid residues collected after reaction under different solvents (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 130°C, 20 min, 1:1 solvent ratio).
- Fig. S3.** Distribution of products in the aqueous phase and organic (GVL) phase during the catalytic conversion of bread waste in GVL/H₂O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 10-20 min, 1:1 solvent ratio).
- Fig. S4.** LA, FA, and HMF distribution in the organic phase and the aqueous phase, and partition coefficients obtained for the catalytic conversion of bread waste in IPA/H₂O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 30 wt% NaCl_(aq) 150°C, 20 min).

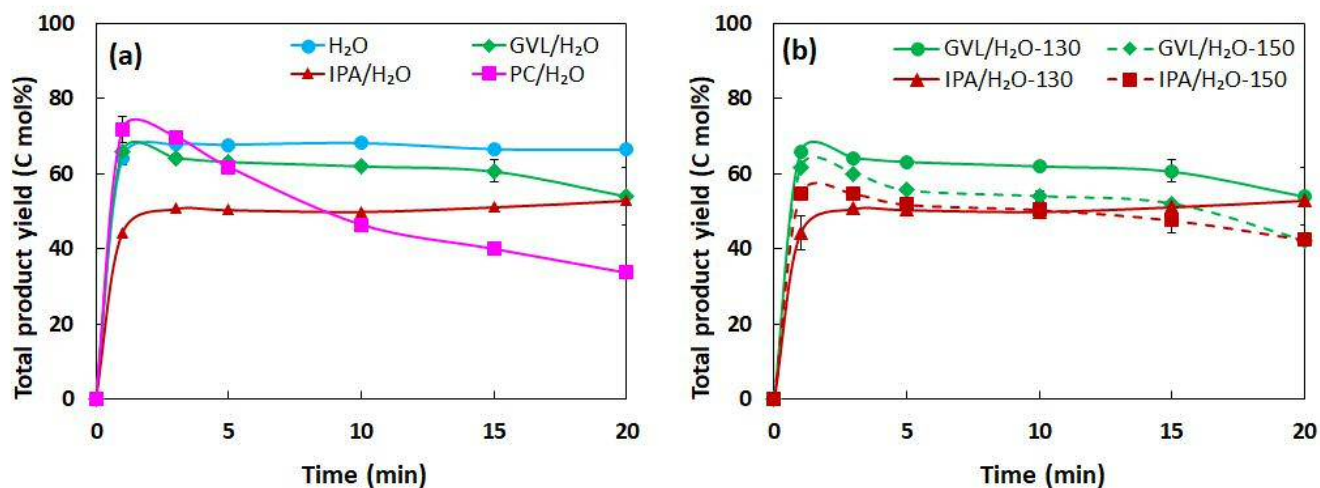


Fig. S1. Total product yields during the catalytic conversion of bread waste under different solvents at (a) at 130°C and (b) at 130°C and 150°C under GVL/H₂O and IPA/H₂O (Reaction conditions: 5 wt% substrate loading, 0.5 M H₂SO₄, 1-20 min, 1:1 solvent ratio).

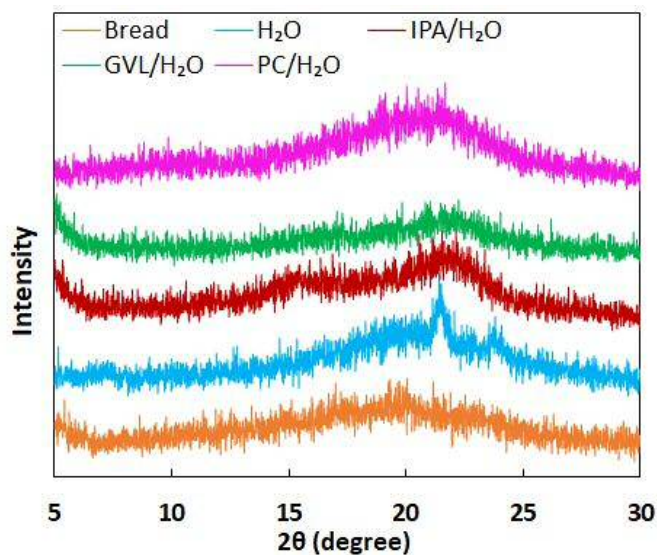


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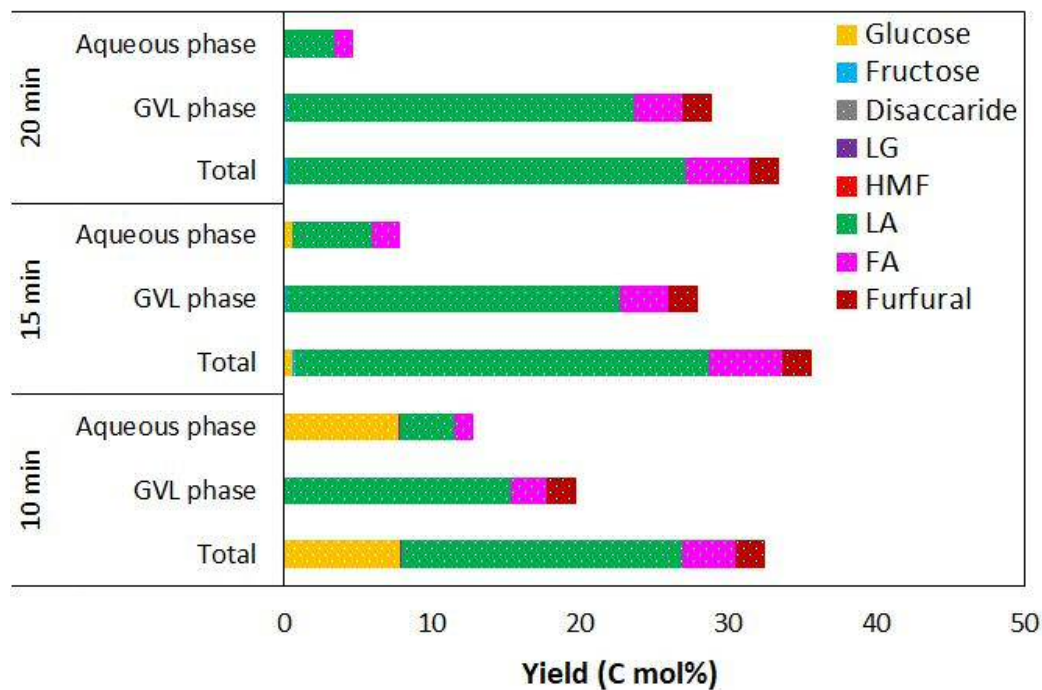


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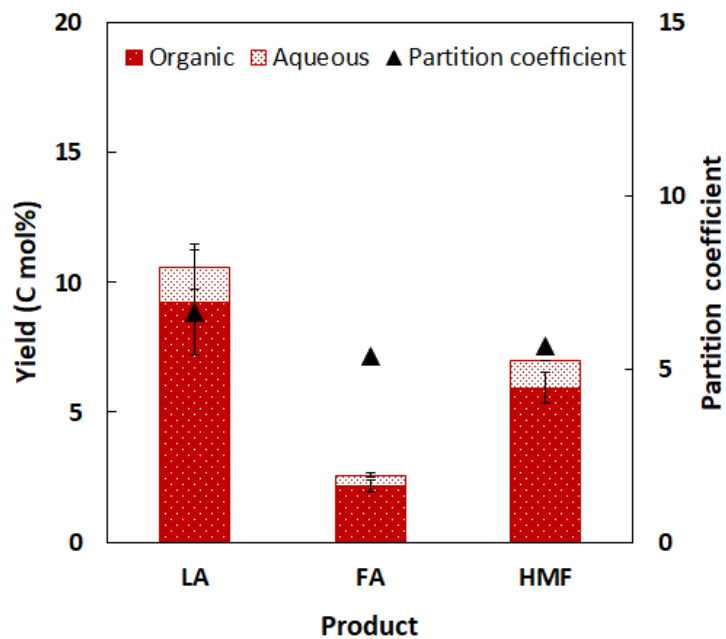


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