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

1 **Critical factors for levulinic acid production from starch-rich food**

2 **waste: Solvent effects, reaction pressure, and phase separation**

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4 Shanta Dutta [a], Iris K.M. Yu [a,b], Jiajun Fan [c], James H. Clark [c], and Daniel C.W. Tsang [a,*]

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7 [a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University,

8 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

9 [b] Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4,

10 85748 Garching, Germany.

11 [c] Green Chemistry Centre of Excellence, Department of Chemistry, University of York,

12 York, YO10 5DD, UK.

13

14 *Corresponding author, dan.tsang@polyu.edu.hk

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 CO_2-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H_2O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H_2O and IPA/H_2O. In PC/H_2O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H_2SO_4), 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/H_2O 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/H_2O (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/H_2O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H_2O 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.

Introduction

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

Levulinic acid (LA) is one of the top bio-derived platform chemicals with various applications, e.g., pharmaceuticals, plasticisers, solvents, fuels, and personal care products.[4-5] Besides, LA serves as a building block for the production of various value-added derivatives such as gamma-valerolactone (GVL),[6] succinic acid, diphenolic acid,[7-8] alkyl levulinates, 2-methyl-tetrahydrofuran, etc.[5] Considering the low cost and high catalytic activity for tandem hydrolysis and dehydration reactions, mineral acids such as H_2SO_4 and HCl are generally used for LA production from diverse biomass feedstock including food waste, paper waste, etc.[9-10] Starch-rich foods such as rice, bread, and potatoes are commonly consumed and constitute a significant proportion of global food waste,[11] which can serve as a potential feedstock for biorefineries. Recent studies demonstrated that catalytic production of sugars and platform chemicals could be an effective technique for recycling/valorising a considerable amount of starch-rich food waste generated globally.[12-13] In this study, bread waste serves as the representative starch-rich feedstock 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 CO_2-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 CO_2-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 H_2O 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 H_2O (DCM/H_2O, 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/H_2O, GVL/H_2O, IPA/H_2O, catalysed by dilute H_2SO_4

97   to investigate how and why an efficient yield of LA could be achieved at moderate reaction

98   conditions using these bio-derived and CO_2-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.

Materials and methods

Bread waste and chemicals

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

Catalytic conversion

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

6

126   experimental observations. To substantiate the experimental results obtained in PC/H$_2$O solvent,

127   additional tests under the selected conditions were conducted using propylene glycol (PG) and

128   water (PG/H$_2$O, 1:1) for comparison.

129   After analysing the results obtained from different monophasic solvent systems, GVL/H$_2$O

130   and IPA/H$_2$O 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 H$_2$SO$_4$ 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 H$_2$SO$_4$ 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
$$Product\ yield\ (C\ mol\%) = \frac{Conc_p\ (mg\ ml^{-1}) \times Vol\ (ml)/MW_p \times C_p}{C_s\ (mol)} \times 100 \quad (1)$$

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/H_2O 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
$$Partition\ coefficient\ (R_x) = \frac{C\ mol\%\ of\ product\ in\ the\ organic\ layer}{C\ mol\%\ of\ product\ in\ the\ aqueous\ layer} \quad (2)$$

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 ^{13}C nuclear magnetic resonance (NMR). Solid ^{13}C 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 ^{13}C NMR using D_2O

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° 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]

Results and discussion

Catalytic conversion of bread waste under bio-derived and CO$_2$-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 CO$_2$-derived co-solvent

176   systems (**Fig. 1a**). For H$_2$O, PC/H$_2$O, and GVL/H$_2$O 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/H$_2$O, 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/H$_2$O (48.1 mol%) and PC/H$_2$O (53.7 mol%)

181   compared to H$_2$O (~30 mol%) and IPA/H$_2$O (9.4 mol%). With increasing reaction duration up to

182   20 min, sugar yield in H$_2$O and IPA/H$_2$O 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/H$_2$O (up to 4.8 mol%) and sharply in PC/H$_2$O

185   (up to 19.6 mol%) (**Fig. 1a**). ^{13}C 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. ^{13}C 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/H$_2$O, 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/H$_2$O further prove the efficient tandem catalysis in

192   PC/H$_2$O. The characteristic peaks for LA and FA were not detectable in IPA/H$_2$O and H$_2$O, while

9

193 low-intensity peaks could be observed for GVL/H$_2$O. Besides, representative solvent peaks [29] were

194 detected in the reacted solutions indicated in **Fig. 2a**.

195   The higher soluble product yields in PC/H$_2$O and GVL/H$_2$O (**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 H$_2$O (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% H$_2$O compared to 100% H$_2$O as solvent.[32] Slower

205 conversion of bread waste was observable in the case of IPA/H$_2$O 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 α(1→4) and α(1→6)

210 glycosidic bonds. ^{13}C 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 ~$2\theta=20°$, and the calculated

231   *CrI* value was ~0.51, whereas solid residues in different solvent systems provided *CrI* values

232   ranging ~0.73-0.78. This also suggested the rapid decomposition of amorphous region of starch

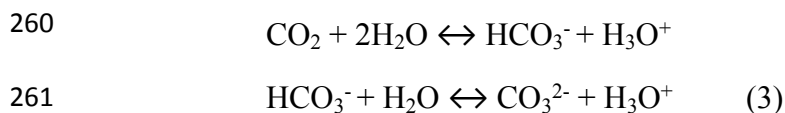233   granules during acid hydrolysis resulting in an increased relative crystallinity.[27]

234

LA yield enhanced by in-vessel high pressure generated in PC/H$_2$O

Comparing different co-solvent systems, PC/H$_2$O was found to be the best for LA production, generating 19.6 mol% after 20 min reaction at 130°C (**Fig. 1a**), which is promising considering mild reaction conditions used in this study and the reported literature results under comparable experimental conditions.[9,39] Under GVL/H$_2$O solvent, sugars depleted gradually during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H$_2$O solvent, sugars started to deplete rapidly during 3-20 min of reaction, and 19.6 mol% LA yield was achieved after 20 min. A significant in-vessel pressure build-up was recorded during reaction in PC/H$_2$O, reaching a maximum ~27 bar at 130°C, 20 min compared to reactions in other solvents (**Fig. 3a**). Compared to the autogenous in-vessel pressure (~13 bar) generated in PC/H$_2$O during 1 min reaction, the reaction pressure level almost doubled (~23-27 bar) during 3-20 min reaction (**Fig. 3b**), which was analogous to rapid sugar consumption and a sharp increase in LA yield (4-19.6 mol%) during 3-20 min. In acidic conditions, PC solvent could decompose into PG and CO$_2$ as reported in the literature.[13,40] Noticeably, ~5-15% solvent loss was recorded for reactions in PC/H$_2$O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the reaction. Besides, ^{13}C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H$_2$O (1 and 20 min) showed peaks at 66.4 and 67.7 ppm representing PG.[29] The PG peaks had comparatively higher intensity after 20 min reaction than 1 min, suggesting that a higher fraction of PC was decomposed to PG, which was consistent with higher CO$_2$ pressure recorded for more prolonged reactions in PC/H$_2$O (**Fig. 3b**).

Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from CO$_2$ generation during catalytic conversion in PC/H$_2$O might enhance the LA production rate. Another influential factor could be the increased acidity due to carbonic acid derived from partial

12

258   dissolution of CO_2 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]

260         $$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$

261         $$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (3)$$

262   The acidity (pH) associated with CO_2 generated during 3-20 min reaction in PC/H_2O was

263   estimated, following the scheme reported in the literature.[43-44] The estimated CO_2-derived pH

264   value for specified reaction conditions was ~3.5, i.e., considerably higher than the H_2SO_4 derived

265   pH (~0.5) in this study. Therefore, CO_2-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/H_2O generated CO_2 pressure more than CO_2-derived acidity during the catalytic

268   conversion of bread waste. To testify this postulation, an additional test using PC/H_2O 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/H_2O (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/H_2O only

275   generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA

276   yield obtained in PC/H_2O, 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.

Intensification of LA yield through phase separation

Among co-solvent systems, PC/H_2O generated the highest LA yield 19.6 mol% at 130°C, and ~9 mol% soluble sugar remained after a 20 min reaction. In contrast, ~47-49 mol% soluble sugar was available after 20 min reaction in GVL/H_2O and IPA/H_2O (**Fig. 1a**), which could be further converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H_2O and IPA/H_2O, conversion of bread waste was conducted at 150°C for 1-20 min reaction duration (**Fig. 4a&b**). As higher temperature provided more energy for the reaction, LA yield increased gradually up to 16.4 mol% in GVL/H_2O (150°C, 20 min) (**Fig. 4b**), which was more than three times higher than the maximum LA yield achieved at 130°C (4.8 mol%, 20 min). The maximum LA yield achieved in IPA/H_2O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than GVL/H_2O system, corroborating the positive role of aprotic GVL solvent in enhancing proton reactivity for less energy-intensive tandem catalysis.[10,30]

The biphasic solvent systems (prepared using 30 wt% $NaCl_{(aq)}$) were further investigated as an intensification scheme to improve the concentration of the target product LA in this study. Promisingly, the concentration of LA at the end of the reaction (150°C, 20 min) increased ~1.6 times in both biphasic GVL/H_2O and IPA/H_2O systems (**Fig. 4c**) compared to analogous monophasic systems. Though total soluble product yields were comparable in the two biphasic systems (~33-35 mol%) (**Fig. S1b**), the distributions of soluble products were distinctive between GVL/H_2O and IPA/H_2O. While biphasic GVL/H_2O selectively generated LA as the main product 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H_2O biphasic contained 10.6 mol% LA, 2.6 mol% FA, ~7 mol% HMF, and 10.2 mol% remaining sugars (glucose and fructose) (**Fig. 4c**). A considerable fraction of HMF present in both monophasic and biphasic IPA/H_2O indicated that 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/H_2O solvent system. In other words, IPA/H_2O could be considered as a potential solvent for

308   HMF production in future investigations. By contrast, in the presence of GVL solvent, H_2SO_4

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/H_2O in this study (26.8 mol%, at 150°C, 20 min)

311   proves the high efficiency of H_2SO_4/GVL/H_2O system for LA production.

312   As GVL/H_2O 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/H_2O,

315   LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H_2O,

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/H_2O (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 (H_2O) and the extraction phase (GVL) to

324   optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H_2O

15

325   biphasic system, catalytic tests were conducted with various ratios of GVL and H_2O (1:1, 1:3, and

326   3:1 of GVL/H_2O). The partition coefficient for LA (R_{LA}) in the GVL/H_2O 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/H_2O 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 H_2O (1:3,

334   GVL/H_2O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-

335   17.1 mol%) when a lower fraction of H_2O (3:1, GVL/H_2O) was applied (**Fig. 5b**). Though the total

336   LA yield increased with a higher fraction of H_2O, the extraction of LA was found to be inefficient.

337   The partition coefficient achieved was only 1.1 (1:3, GVL/H_2O), 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/H_2O) 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/H_2O 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/H_2O 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 H_2SO_4 for bread

350   waste conversion, an increase in LA yield was observed compared to the reaction in the presence

351   of H_2SO_4 without salt addition. These observations indicate that NaCl alone could not catalyse the

352   desired reaction yet it may act synergistically with H_2SO_4 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 H_2SO_4 together with simultaneous efficient extraction of LA into GVL could account

356   for the high LA yield obtained in the GVL/H_2O biphasic system.

357   Moreover, the recyclability of the aqueous phase containing H_2SO_4 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 H_2SO_4. 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/H_2O, 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/H_2O (150°C, 15

371 min, 1:3 solvent ratio) (**Fig. 5c**). Using 1:1 GVL/H_2O, 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/H_2O 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/H_2O.

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/H_2O (130°C, 20 min) and GVL/H_2O 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 studies[49-50] 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/H_2O biphasic solvent was investigated and discussed in the

391 previous section. For PC/H_2O 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 CO_2 is beneficial for process economy

395   and environmental sustainability in terms of CO_2 utilisation. In the application of PC solvent, the

396   derived CO_2 after reaction can be captured and recycled for PC production or other CO_2 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   recovery[52] 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.

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 CO_2-derived

408   co-solvents in this study, i.e., PC/H_2O, GVL/H_2O, IPA/H_2O, could facilitate H_2SO_4 catalysed

409   tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency.

410   PC/H_2O solvent was the most efficient for LA production using moderate reaction conditions,

411   which could be attributed to the CO_2 pressure generated *in situ* through solvent (PC) degradation.

412   Besides, catalytic performance could be significantly enhanced in GVL/H_2O and IPA/H_2O using

413   the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the

414   final concentration of LA. GVL/H_2O 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 CO_2-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

Supplementary information

420 The supplementary information is available online.

421

Conflicts of interest

423 The authors declare no conflict of interest.

424

Acknowledgements

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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

4 Shanta Dutta [a], Iris K.M. Yu [a,b], Jiajun Fan [c], James H. Clark [c], and Daniel C.W. Tsang [a,*]

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6

7 [a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University,

8 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

9 [b] Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4,

10 85748 Garching, Germany.

11 [c] Green Chemistry Centre of Excellence, Department of Chemistry, University of York,

12 York, YO10 5DD, UK.

13

14 *Corresponding author, dan.tsang@polyu.edu.hk

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 CO_2-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H_2O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H_2O and IPA/H_2O. In PC/H_2O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H_2SO_4), 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/H_2O 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/H_2O (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/H_2O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H_2O 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.

Introduction

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

Levulinic acid (LA) is one of the top bio-derived platform chemicals with various applications, e.g., pharmaceuticals, plasticisers, solvents, fuels, and personal care products.[4-5] Besides, LA serves as a building block for the production of various value-added derivatives such as gamma-valerolactone (GVL),[6] succinic acid, diphenolic acid,[7-8] alkyl levulinates, 2-methyl-tetrahydrofuran, etc.[5] Considering the low cost and high catalytic activity for tandem hydrolysis and dehydration reactions, mineral acids such as H_2SO_4 and HCl are generally used for LA production from diverse biomass feedstock including food waste, paper waste, etc.[9-10] Starch-rich foods such as rice, bread, and potatoes are commonly consumed and constitute a significant proportion of global food waste,[11] which can serve as a potential feedstock for biorefineries. Recent studies demonstrated that catalytic production of sugars and platform chemicals could be an effective technique for recycling/valorising a considerable amount of starch-rich food waste generated globally.[12-13] In this study, bread waste serves as the representative starch-rich feedstock 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 CO_2-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 CO_2-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 H_2O 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 H_2O (DCM/H_2O, 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/H_2O, GVL/H_2O, IPA/H_2O, catalysed by dilute H_2SO_4

97   to investigate how and why an efficient yield of LA could be achieved at moderate reaction

98   conditions using these bio-derived and CO_2-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.

Materials and methods

Bread waste and chemicals

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

Catalytic conversion

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

6

126   experimental observations. To substantiate the experimental results obtained in PC/H_2O solvent,

127   additional tests under the selected conditions were conducted using propylene glycol (PG) and

128   water (PG/H_2O, 1:1) for comparison.

129   After analysing the results obtained from different monophasic solvent systems, GVL/H_2O

130   and IPA/H_2O 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 H_2SO_4 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 H_2SO_4 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
$$Product\ yield\ (C\ mol\%) = \frac{Conc_p\ (mg\ ml^{-1}) \times Vol\ (ml)/MW_p \times C_p}{C_s\ (mol)} \times 100 \quad (1)$$

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/H$_2$O 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
$$Partition\ coefficient\ (R_x) = \frac{C\ mol\%\ of\ product\ in\ the\ organic\ layer}{C\ mol\%\ of\ product\ in\ the\ aqueous\ layer} \quad (2)$$

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 ^{13}C nuclear magnetic resonance (NMR). Solid ^{13}C 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 ^{13}C NMR using D$_2$O

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° 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]

Results and discussion

Catalytic conversion of bread waste under bio-derived and CO$_2$-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 CO$_2$-derived co-solvent

176   systems (**Fig. 1a**). For H$_2$O, PC/H$_2$O, and GVL/H$_2$O 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/H$_2$O, 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/H$_2$O (48.1 mol%) and PC/H$_2$O (53.7 mol%)

181   compared to H$_2$O (~30 mol%) and IPA/H$_2$O (9.4 mol%). With increasing reaction duration up to

182   20 min, sugar yield in H$_2$O and IPA/H$_2$O 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/H$_2$O (up to 4.8 mol%) and sharply in PC/H$_2$O

185   (up to 19.6 mol%) (**Fig. 1a**). ^{13}C 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. ^{13}C 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/H$_2$O, 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/H$_2$O further prove the efficient tandem catalysis in

192   PC/H$_2$O. The characteristic peaks for LA and FA were not detectable in IPA/H$_2$O and H$_2$O, while

193   low-intensity peaks could be observed for GVL/H_2O. Besides, representative solvent peaks [29] were

194   detected in the reacted solutions indicated in **Fig. 2a**.

195   The higher soluble product yields in PC/H_2O and GVL/H_2O (**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 H_2O (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% H_2O compared to 100% H_2O as solvent.[32] Slower

205   conversion of bread waste was observable in the case of IPA/H_2O 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 α(1→4) and α(1→6)

210   glycosidic bonds. ^{13}C 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
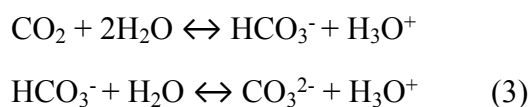
216   post-reaction solid residues shifted toward 98-103 ppm, presenting comparatively sharp peaks

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 ~$2\theta=20°$, and the calculated

231   *CrI* value was ~0.51, whereas solid residues in different solvent systems provided *CrI* values

232   ranging ~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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LA yield enhanced by in-vessel high pressure generated in PC/H$_2$O

Comparing different co-solvent systems, PC/H$_2$O was found to be the best for LA production, generating 19.6 mol% after 20 min reaction at 130°C (**Fig. 1a**), which is promising considering mild reaction conditions used in this study and the reported literature results under comparable experimental conditions.[9,39] Under GVL/H$_2$O solvent, sugars depleted gradually during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H$_2$O solvent, sugars started to deplete rapidly during 3-20 min of reaction, and 19.6 mol% LA yield was achieved after 20 min. A significant in-vessel pressure build-up was recorded during reaction in PC/H$_2$O, reaching a maximum ~27 bar at 130°C, 20 min compared to reactions in other solvents (**Fig. 3a**). Compared to the autogenous in-vessel pressure (~13 bar) generated in PC/H$_2$O during 1 min reaction, the reaction pressure level almost doubled (~23-27 bar) during 3-20 min reaction (**Fig. 3b**), which was analogous to rapid sugar consumption and a sharp increase in LA yield (4-19.6 mol%) during 3-20 min. In acidic conditions, PC solvent could decompose into PG and CO$_2$ as reported in the literature.[13,40] Noticeably, ~5-15% solvent loss was recorded for reactions in PC/H$_2$O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the reaction. Besides, ^{13}C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H$_2$O (1 and 20 min) showed peaks at 66.4 and 67.7 ppm representing PG.[29] The PG peaks had comparatively higher intensity after 20 min reaction than 1 min, suggesting that a higher fraction of PC was decomposed to PG, which was consistent with higher CO$_2$ pressure recorded for more prolonged reactions in PC/H$_2$O (**Fig. 3b**).

Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from CO$_2$ generation during catalytic conversion in PC/H$_2$O might enhance the LA production rate. Another influential factor could be the increased acidity due to carbonic acid derived from partial

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258 dissolution of CO_2 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]

260 $$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$

261 $$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (3)$$

262 The acidity (pH) associated with CO_2 generated during 3-20 min reaction in PC/H_2O was

263 estimated, following the scheme reported in the literature.[43-44] The estimated CO_2-derived pH

264 value for specified reaction conditions was ~3.5, i.e., considerably higher than the H_2SO_4 derived

265 pH (~0.5) in this study. Therefore, CO_2-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/H_2O generated CO_2 pressure more than CO_2-derived acidity during the catalytic

268 conversion of bread waste. To testify this postulation, an additional test using PC/H_2O 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/H_2O (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/H_2O only

275 generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA

276 yield obtained in PC/H_2O, 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.

Intensification of LA yield through phase separation

Among co-solvent systems, PC/H_2O generated the highest LA yield 19.6 mol% at 130°C, and ~9 mol% soluble sugar remained after a 20 min reaction. In contrast, ~47-49 mol% soluble sugar was available after 20 min reaction in GVL/H_2O and IPA/H_2O (**Fig. 1a**), which could be further converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H_2O and IPA/H_2O, conversion of bread waste was conducted at 150°C for 1-20 min reaction duration (**Fig. 4a&b**). As higher temperature provided more energy for the reaction, LA yield increased gradually up to 16.4 mol% in GVL/H_2O (150°C, 20 min) (**Fig. 4b**), which was more than three times higher than the maximum LA yield achieved at 130°C (4.8 mol%, 20 min). The maximum LA yield achieved in IPA/H_2O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than GVL/H_2O system, corroborating the positive role of aprotic GVL solvent in enhancing proton reactivity for less energy-intensive tandem catalysis.[10,30]

The biphasic solvent systems (prepared using 30 wt% $NaCl_{(aq)}$) were further investigated as an intensification scheme to improve the concentration of the target product LA in this study. Promisingly, the concentration of LA at the end of the reaction (150°C, 20 min) increased ~1.6 times in both biphasic GVL/H_2O and IPA/H_2O systems (**Fig. 4c**) compared to analogous monophasic systems. Though total soluble product yields were comparable in the two biphasic systems (~33-35 mol%) (**Fig. S1b**), the distributions of soluble products were distinctive between GVL/H_2O and IPA/H_2O. While biphasic GVL/H_2O selectively generated LA as the main product 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H_2O biphasic contained 10.6 mol% LA, 2.6 mol% FA, ~7 mol% HMF, and 10.2 mol% remaining sugars (glucose and fructose) (**Fig. 4c**). A considerable fraction of HMF present in both monophasic and biphasic IPA/H_2O indicated that the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely

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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/H_2O solvent system. In other words, IPA/H_2O could be considered as a potential solvent for

308 HMF production in future investigations. By contrast, in the presence of GVL solvent, H_2SO_4

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/H_2O in this study (26.8 mol%, at 150°C, 20 min)

311 proves the high efficiency of H_2SO_4/GVL/H_2O system for LA production.

312   As GVL/H_2O 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/H_2O,

315 LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H_2O,

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/H_2O (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 (H_2O) and the extraction phase (GVL) to

324 optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H_2O

325   biphasic system, catalytic tests were conducted with various ratios of GVL and H_2O (1:1, 1:3, and

326   3:1 of GVL/H_2O). The partition coefficient for LA (R_{LA}) in the GVL/H_2O 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/H_2O 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 H_2O (1:3,

334   GVL/H_2O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-

335   17.1 mol%) when a lower fraction of H_2O (3:1, GVL/H_2O) was applied (**Fig. 5b**). Though the total

336   LA yield increased with a higher fraction of H_2O, the extraction of LA was found to be inefficient.

337   The partition coefficient achieved was only 1.1 (1:3, GVL/H_2O), 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/H_2O) 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/H_2O 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/H_2O biphasic system, additional tests were performed under the selected reaction conditions.

16

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 H_2SO_4 for bread

350   waste conversion, an increase in LA yield was observed compared to the reaction in the presence

351   of H_2SO_4 without salt addition. These observations indicate that NaCl alone could not catalyse the

352   desired reaction yet it may act synergistically with H_2SO_4 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 H_2SO_4 together with simultaneous efficient extraction of LA into GVL could account

356   for the high LA yield obtained in the GVL/H_2O biphasic system.

357   Moreover, the recyclability of the aqueous phase containing H_2SO_4 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 H_2SO_4. 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/H_2O, 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/H_2O (150°C, 15

371   min, 1:3 solvent ratio) (**Fig. 5c**). Using 1:1 GVL/H_2O, 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/H_2O 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/H_2O.

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/H_2O (130°C, 20 min) and GVL/H_2O 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 studies[49-50] 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/H_2O biphasic solvent was investigated and discussed in the

391   previous section. For PC/H_2O 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 CO_2 is beneficial for process economy

395   and environmental sustainability in terms of CO_2 utilisation. In the application of PC solvent, the

396   derived CO_2 after reaction can be captured and recycled for PC production or other CO_2 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   recovery[52] 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.

Conclusions

405

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 CO_2-derived

408   co-solvents in this study, i.e., PC/H_2O, GVL/H_2O, IPA/H_2O, could facilitate H_2SO_4 catalysed

409   tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency.

410   PC/H_2O solvent was the most efficient for LA production using moderate reaction conditions,

411   which could be attributed to the CO_2 pressure generated *in situ* through solvent (PC) degradation.

412   Besides, catalytic performance could be significantly enhanced in GVL/H_2O and IPA/H_2O using

413   the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the

414   final concentration of LA. GVL/H_2O 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 CO_2-derived

19

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

425   **Acknowledgements**

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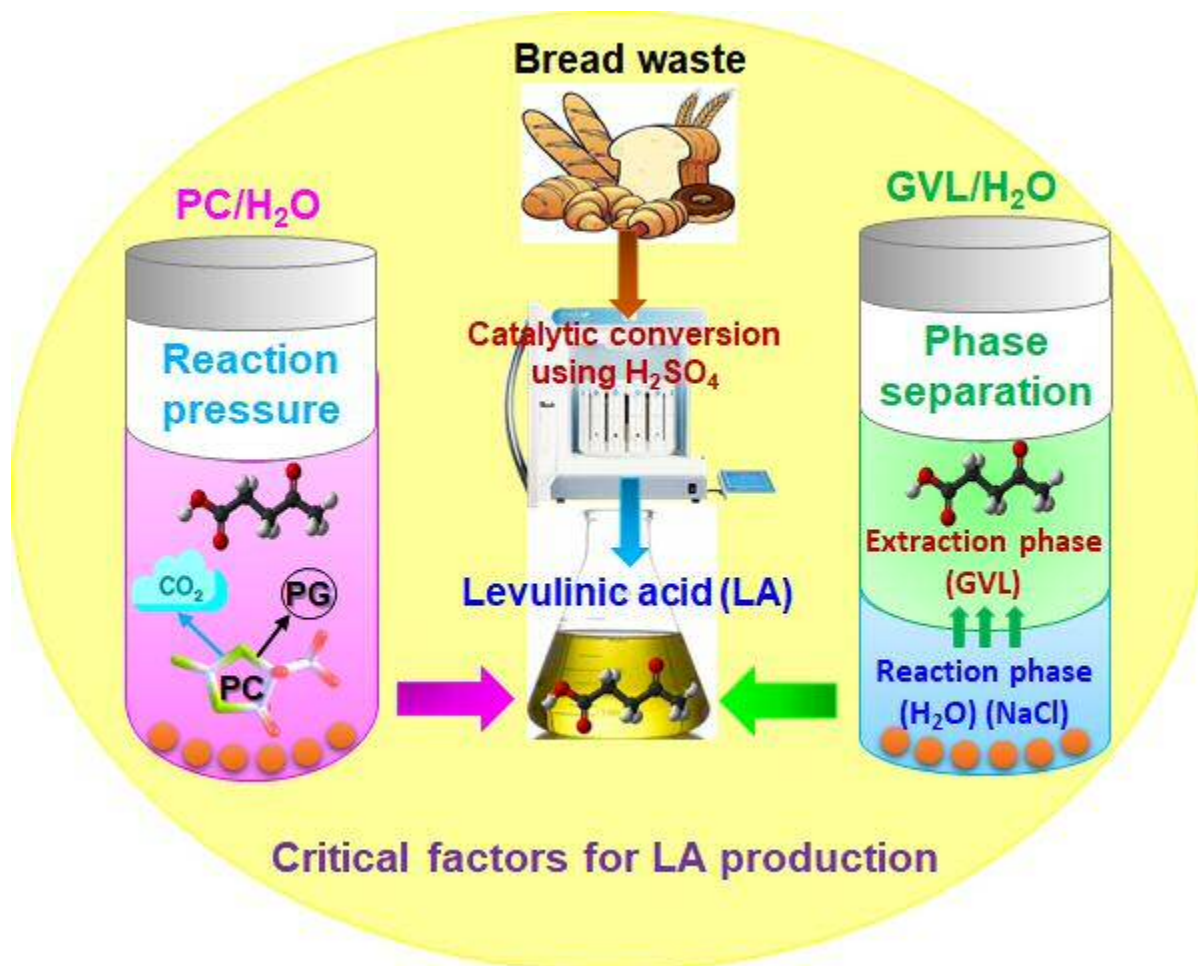
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614

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
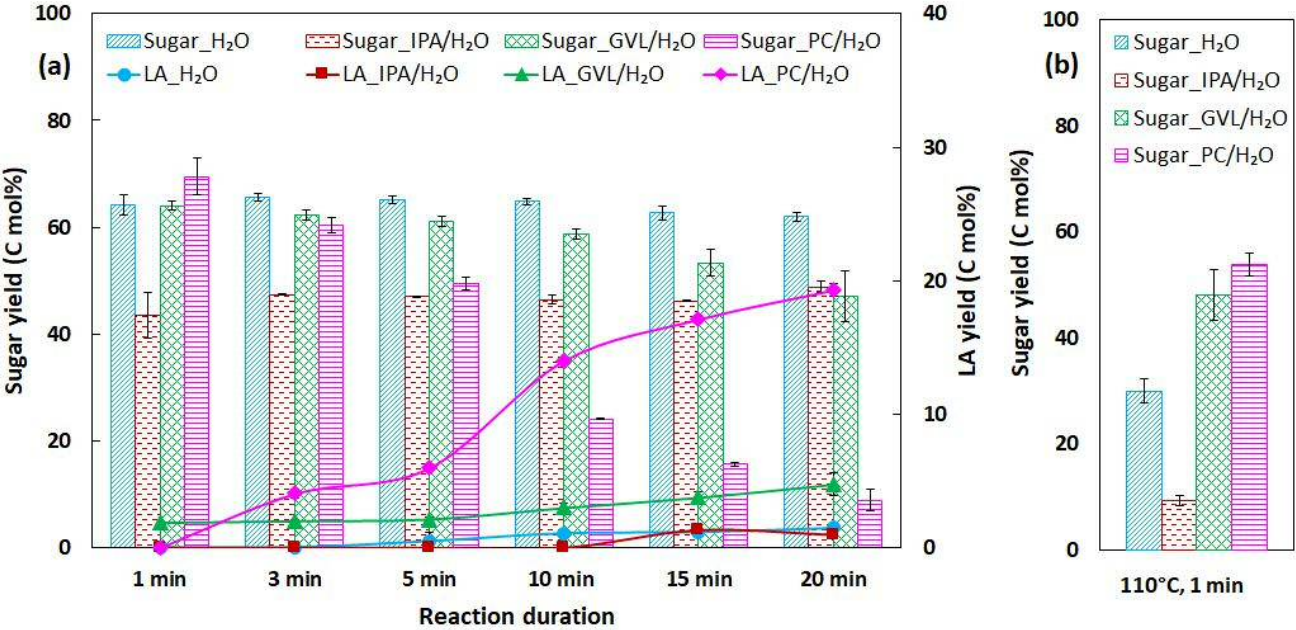
List of figures:

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 H_2SO_4, 130°C, 1:1 solvent ratio).
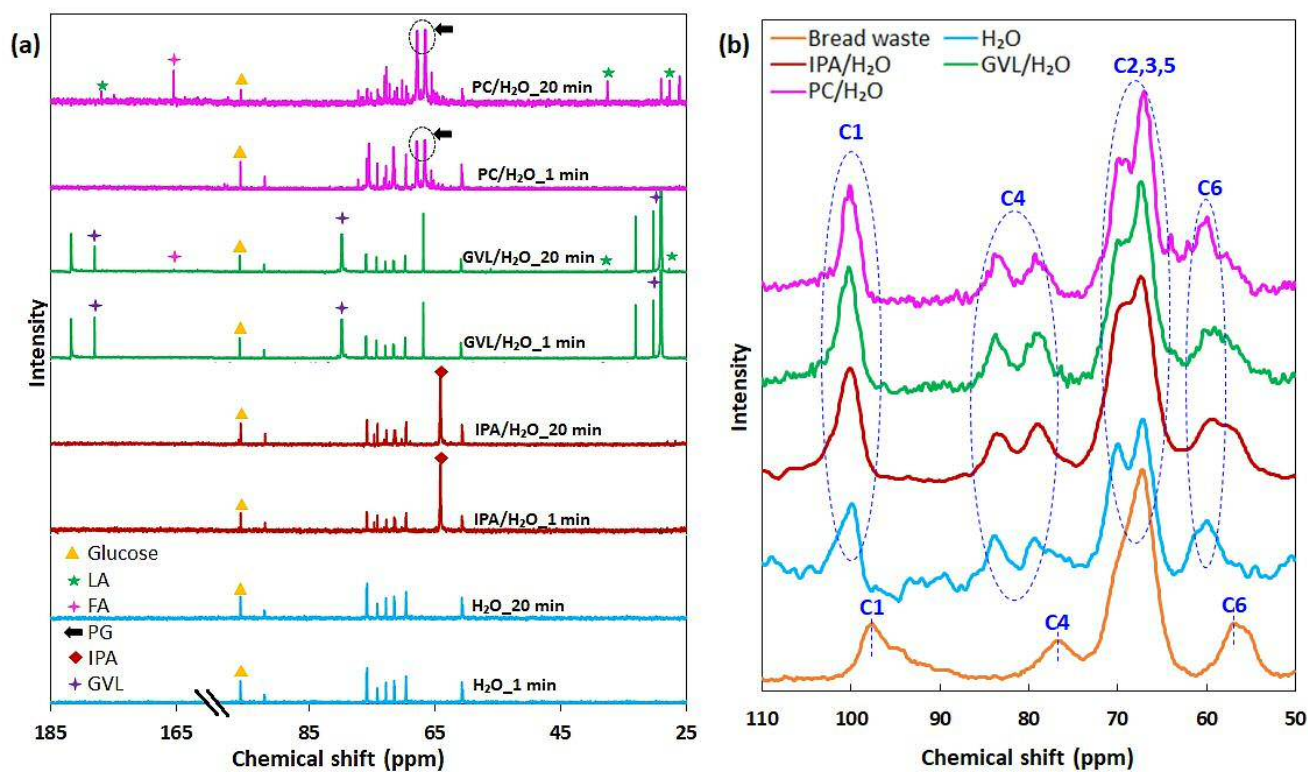
Fig. 2. (a) ^{13}C NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M H_2SO_4, 130°C, 1 min & 20 min, 1:1 solvent ratio), (b) ^{13}C solid-state NMR spectra of untreated bread waste and solid residues collected 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).
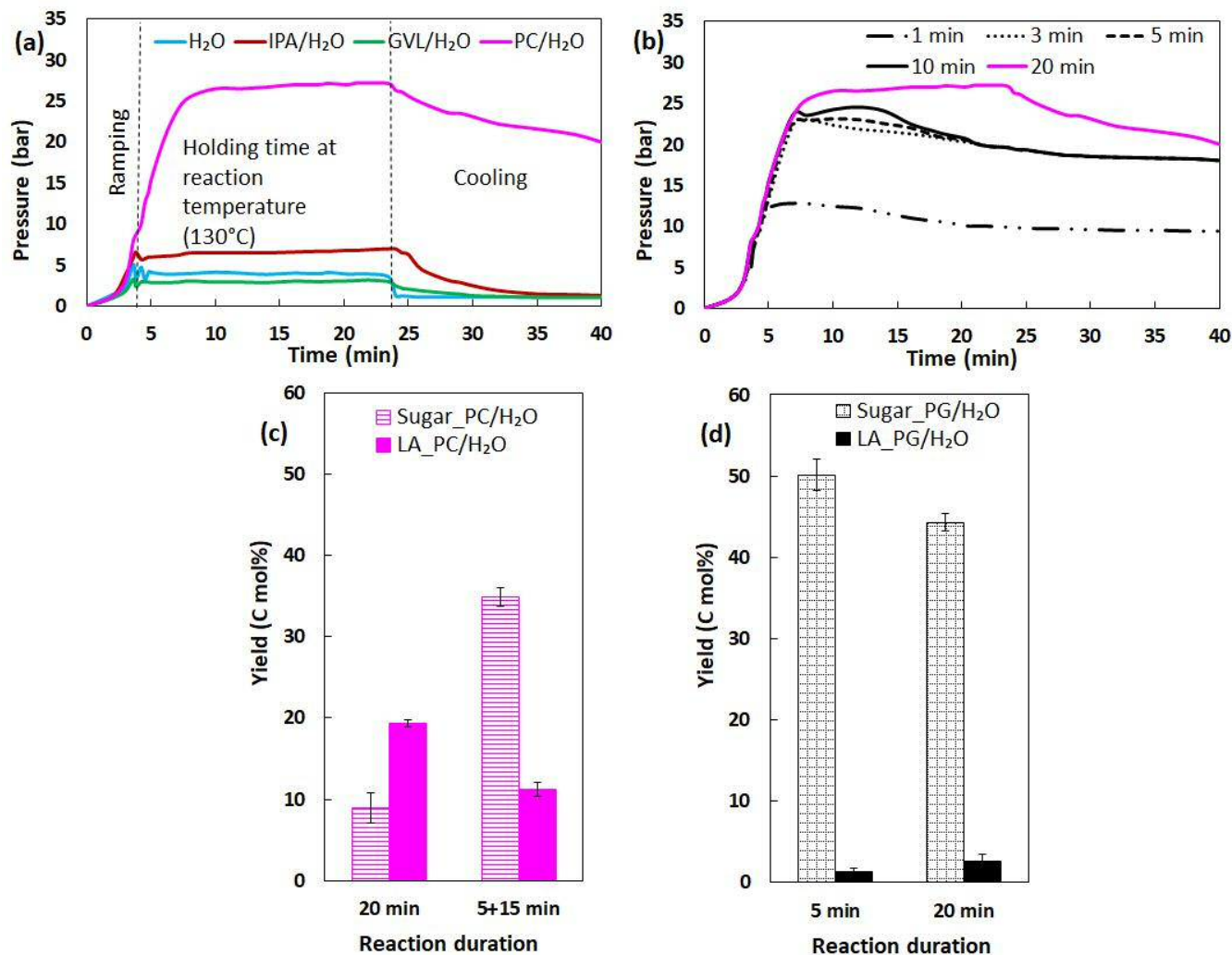
Fig. 3. (a) Pressure profile during the catalytic conversion of bread waste in different solvents for 20 min reaction, (b) pressure profile in PC/H_2O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H_2O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H_2O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 130°C, 1:1 solvent ratio).
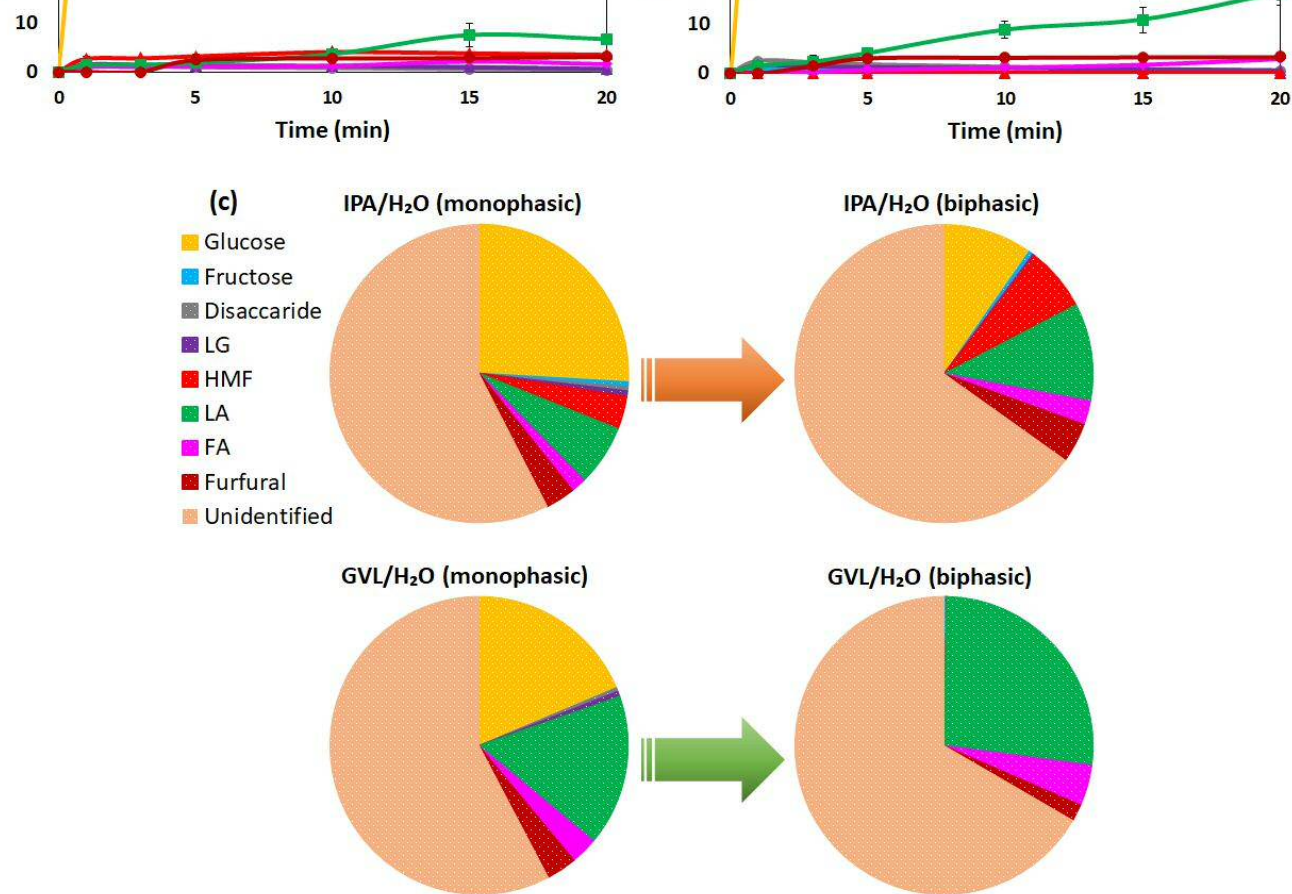
Fig. 4. Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H_2O (monophasic) and (b) GVL/H_2O (monophasic); (c) comparative product yields in IPA/H_2O and GVL/H_2O monophasic and biphasic medium (30 wt% $NaCl_{(aq)}$) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 1:1 solvent ratio).
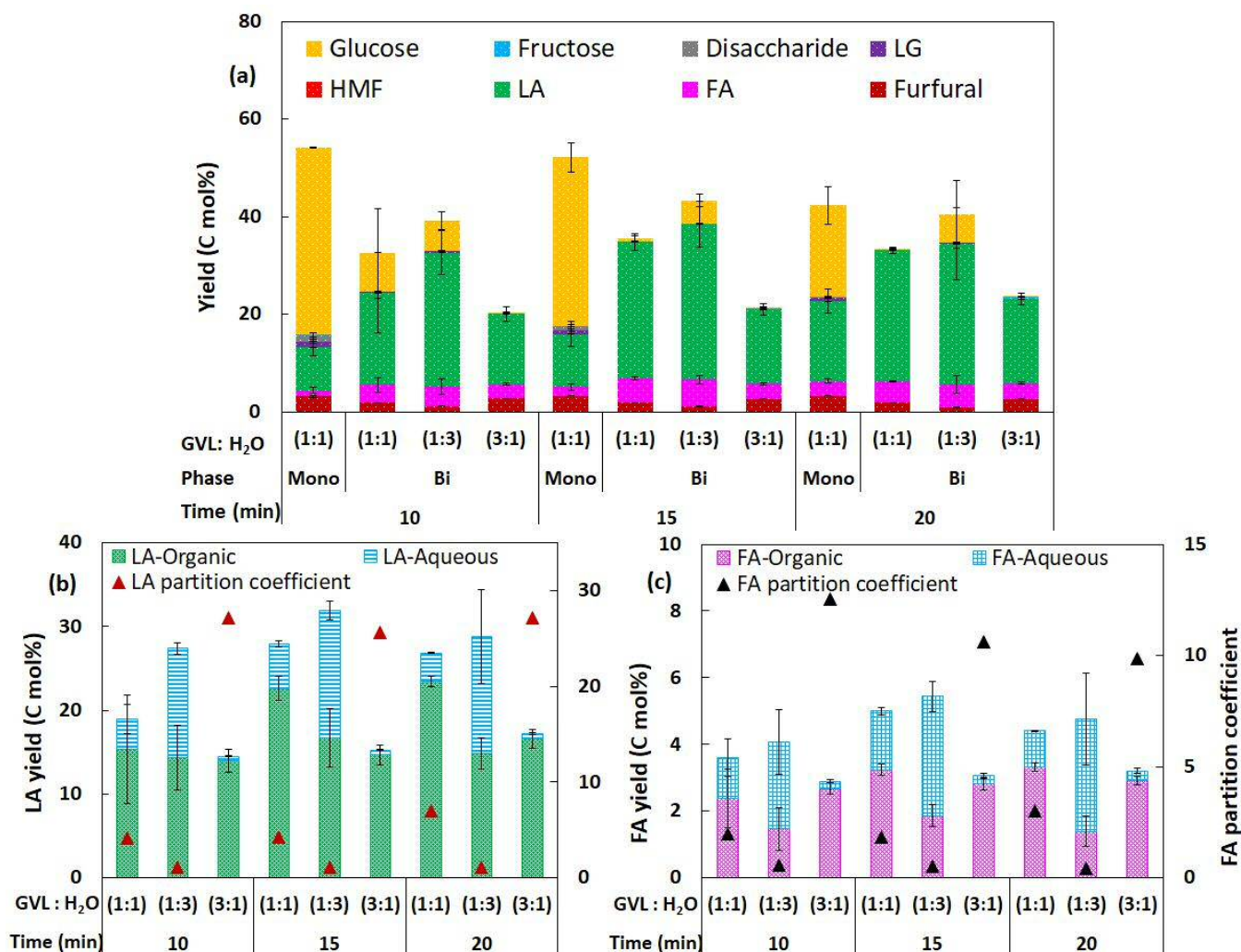
Fig. 5. (a) Product yields during the catalytic conversion of bread waste in GVL/H_2O monophasic and biphasic medium comprising different solvent ratios; (b) LA and (c) FA distribution in the organic and aqueous phase and partition coefficients obtained for the catalytic conversion of bread waste in GVL/H_2O 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 H_2SO_4, 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/H_2O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 30 wt% $NaCl_{(aq)}$ 150°C, 15 min, solvent ratio 1:1).

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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/H$_2$O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H$_2$O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H$_2$O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H$_2$SO$_4$, 130°C, 1:1 solvent ratio).

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Fig. 4. Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H_2O (monophasic) and (b) GVL/H_2O (monophasic); (c) comparative product yields in IPA/H_2O and GVL/H_2O monophasic and biphasic medium (30 wt% NaCl$_{(aq)}$) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 1:1 solvent ratio).

Fig. 5. (a) Product yields during the catalytic conversion of bread waste in GVL/H_2O 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/H_2O biphasic medium comprising different solvent ratio (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 30 wt% $NaCl_{(aq)}$ 150°C, 10-20 min).
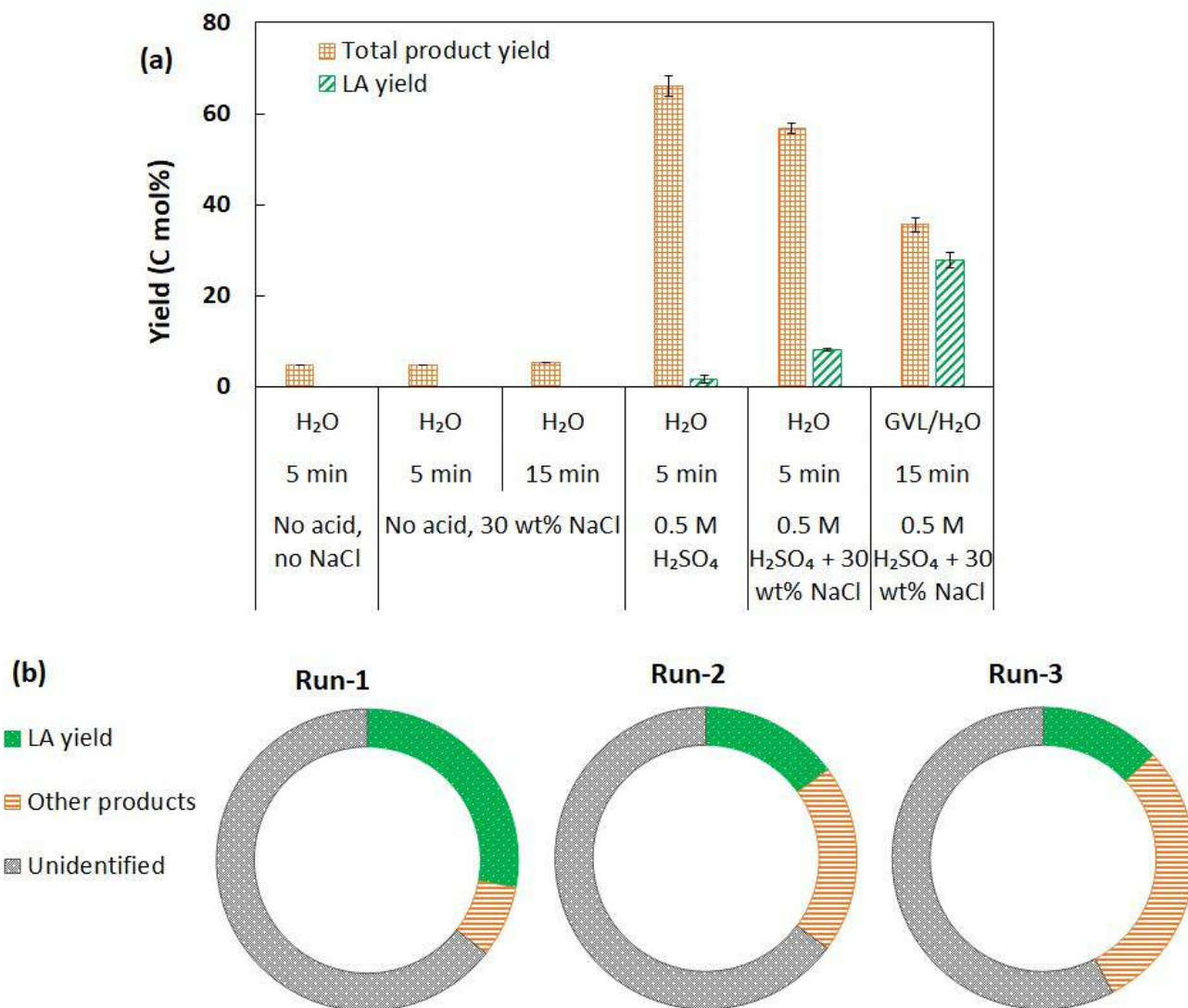
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Fig. 6. (a) LA yield and total product yield under different reaction conditions (Reaction conditions: 5 wt% substrate loading, 150°C), (b) LA yield and other products (sugar+HMF+furfural) of consecutive runs in GVL/H_2O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 30 wt% $NaCl_{(aq)}$ 150°C, 15 min, solvent ratio 1:1).

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

Substrate	Reaction conditions	Catalyst	LA yield based on total organic carbon (mol%)	LA yield based on weight of substrate (%)	LA yiel... to the... yiel...
Bread waste	130°C, 20 min, H_2O	0.5 M H_2SO_4	1.5	1.2	
	130°C, 20 min, IPA/H_2O		1.0	0.8	
	130°C, 20 min, GVL/H_2O		4.8	3.8	
	130°C, 20 min, PC/H_2O		19.6	**15.5**	
	150°C, 20 min, IPA/H_2O (mono)		6.6	5.3	
	150°C, 20 min, IPA/H_2O (bi)		10.6	8.5	
	150°C, 15 min, GVL/H_2O (mono)		10.9	8.8	
	150°C, 15 min, GVL/H_2O (bi)		27.9	**22.4**	
	150°C, 20 min, GVL/H_2O (mono)		16.4	13.2	
	150°C, 20 min, GVL/H_2O (bi)		26.8	**21.6**	
Bread	130°C, 8 h	1.5 ml 5 M H_2SO_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_2SO_4	-	47.5	
Sorghum grain	200°C, 40 min	8% H_2SO_4		32.6	

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Supplementary Information

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

Shanta Dutta [a], Iris K.M. Yu [a,b], Jiajun Fan [c], James H. Clark [c], and Daniel C.W. Tsang [a,*]

[a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

[b] Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany.

[c] Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK.

*Corresponding author, dan.tsang@polyu.edu.hk
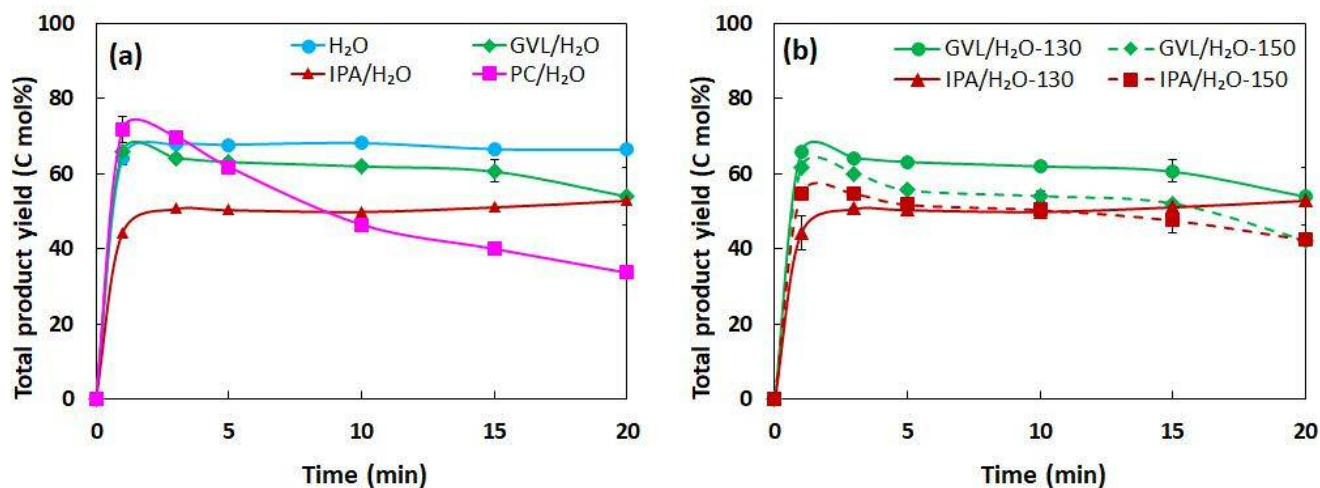
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Fig. S1. Total product yields during the catalytic conversion of bread waste under different solvents at (a) at 130°C and (b) at 130°C and 150°C under GVL/H_2O and IPA/H_2O (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 1-20 min, 1:1 solvent ratio).
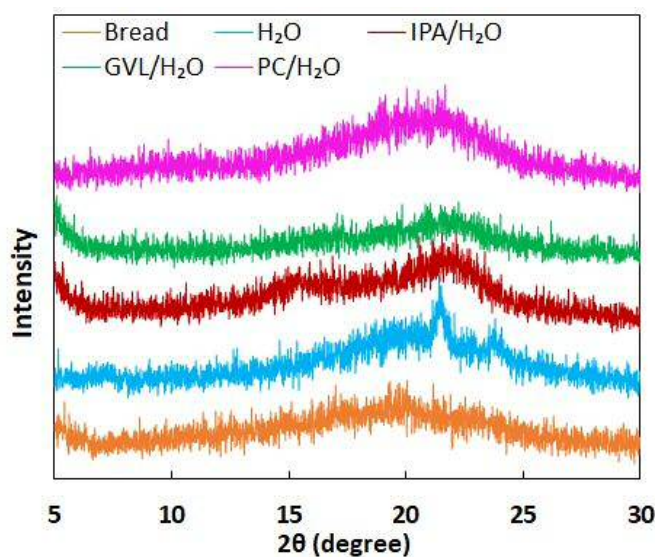

Fig. S2. XRD pattern of untreated bread waste and solid residues collected after reaction under different solvents (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 130°C, 20 min, 1:1 solvent ratio).
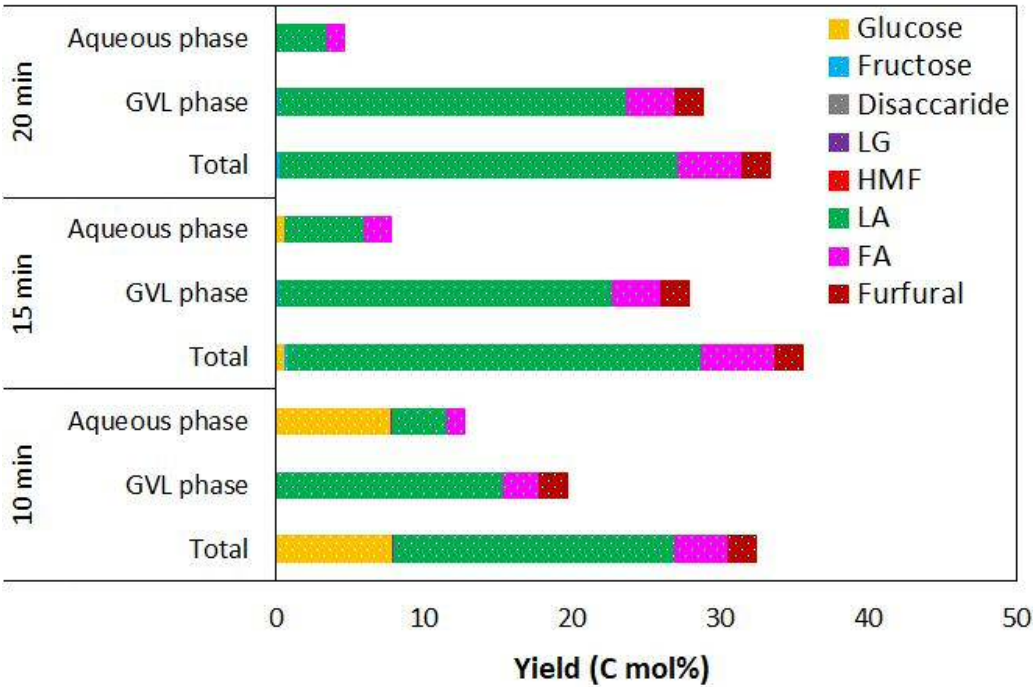
Fig. S3. Distribution of products in the aqueous phase and organic (GVL) phase during the catalytic conversion of bread waste in GVL/H_2O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 30 wt% $NaCl_{(aq)}$ 150°C, 10-20 min, 1:1 solvent ratio).
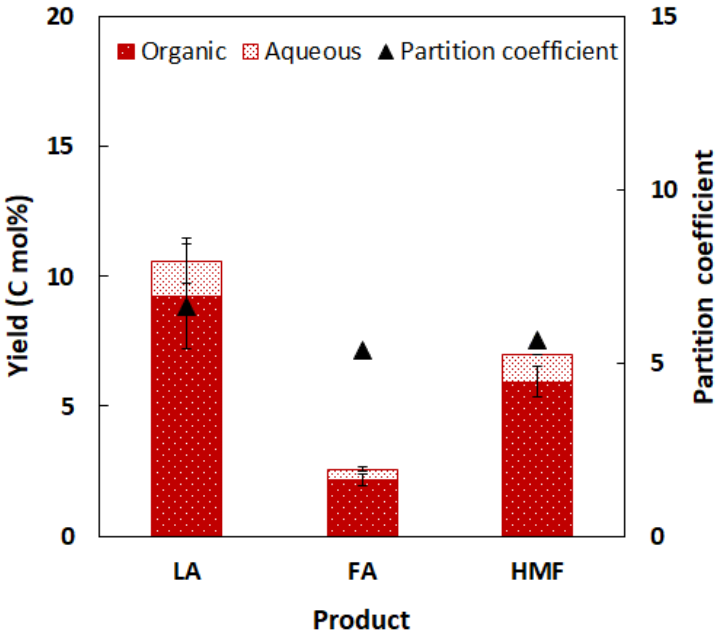

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Fig. S4. LA, FA, and HMF distribution in the organic phase and the aqueous phase, and partition coefficients obtained for the catalytic conversion of bread waste in IPA/H_2O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H_2SO_4, 30 wt% $NaCl_{(aq)}$ 150°C, 20 min).