



Green  
Chemistry

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

Journal:	<i>Green Chemistry</i>
Manuscript ID	GC-ART-06-2021-001948.R2
Article Type:	Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Dutta, Shanta; The Hong Kong Polytechnic University, Civil and Environmental Engineering Yu, Iris; Technical University of Munich, Chemistry Fan, Jiajun; University of York, Chemistry Clark, James; University of York, Chemistry Tsang, Dan; The Hong Kong Polytechnic University, Civil and Environmental Engineering

SCHOLARONE™  
Manuscripts

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

Shanta Dutta <sup>a</sup>, Iris K.M. Yu <sup>a,b</sup>, Jiajun Fan <sup>c</sup>, James H. Clark <sup>c</sup>, and Daniel C.W. Tsang <sup>a,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

<sup>b</sup> Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany.

<sup>c</sup> Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK.

\*Corresponding author, [dan.tsang@polyu.edu.hk](mailto: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<sub>2</sub>-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H<sub>2</sub>O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O. In PC/H<sub>2</sub>O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H<sub>2</sub>SO<sub>4</sub>), 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<sub>2</sub>O through phase separation using NaCl (30 wt%<sub>(aq)</sub>). 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<sub>2</sub>O (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<sub>2</sub>O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H<sub>2</sub>O 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.<sup>1</sup> Such an enormous  
43 amount of food waste requires proper handling to minimise pollution risks and be diverted from  
44 landfill disposal.<sup>2</sup> 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.<sup>3</sup>

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.<sup>4-5</sup>  
49 Besides, LA serves as a building block for the production of various value-added derivatives such  
50 as gamma-valerolactone (GVL),<sup>6</sup> succinic acid, diphenolic acid,<sup>7-8</sup> alkyl levulinates, 2-methyl-  
51 tetrahydrofuran, etc.<sup>5</sup> Considering the low cost and high catalytic activity for tandem hydrolysis  
52 and dehydration reactions, mineral acids such as H<sub>2</sub>SO<sub>4</sub> and HCl are generally used for LA  
53 production from diverse biomass feedstock including food waste, paper waste, etc.<sup>9-10</sup> Starch-rich  
54 foods such as rice, bread, and potatoes are commonly consumed and constitute a significant  
55 proportion of global food waste,<sup>11</sup> 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.<sup>12-13</sup> In this study, bread waste serves as the representative starch-rich feedstock  
59 for the catalytic production of LA.

Appropriate reaction conditions and solvent selection are critical for selective and cost-effective LA production.<sup>14</sup> As the greenest and environmentally benign solvent, water has been used as a reaction medium for LA synthesis. However, harsh reaction conditions, i.e., high temperature and acidity, are required when using water as the reaction medium resulting in an energy-intensive process and high byproduct (humin) formation.<sup>15</sup> The selection of a suitable solvent is necessary, as it not only serves as a reaction medium, but also influences the catalytic process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the byproduct formation, etc.<sup>13,16</sup> Owing to the need for selective and high-efficiency chemical synthesis, various organic solvents as reaction medium have been widely investigated, such as dimethylsulfoxide (DMSO),<sup>9</sup> tetrahydrofuran (THF), dimethylformamide (DMF),<sup>7</sup> GVL, acetone, etc.<sup>10,17</sup> However, conventional organic solvents DMSO, DMF, THF, etc., are widely considered “non-green” due to their direct or indirect detrimental effects on the natural environment and human health and safety. Therefore, the use of alternative “green” solvents, and especially those which are renewable and bio-derived (GVL, alcohols, etc.) or CO<sub>2</sub>-derived (propylene carbonate (PC), dimethyl carbonate (DMC), etc.), are recommended for future applications.<sup>18-19</sup> Furthermore, enhanced catalytic conversion of biowaste using these bio-derived and CO<sub>2</sub>-derived solvents was reported in recent studies,<sup>10,13,20</sup> yet their influences should be evaluated in comparable conditions to validate their efficiency and elucidate the critical factors for catalytic LA production.

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

be using the biphasic solvent system comprising two immiscible layers. The aqueous layer contains the acid catalyst and serves as the reactive phase, while the organic layer acts as the extractive phase, facilitating simultaneous production and extraction of LA, which might enhance LA yield and selectivity.<sup>21-22</sup> For instance, a recent study on the conversion of remnant algal biomass reported a significant enhancement of hydroxymethylfurfural (HMF) and LA yield using acidic ZSM-5 zeolite as a heterogeneous catalyst when utilising a biphasic solvent system composed of methyl isobutyl ketone (MIBK) and H<sub>2</sub>O with NaCl as the phase modifier.<sup>23</sup> Another study achieved a ~4 fold increase in LA yield from rice straw using a biphasic reaction medium containing dichloromethane (DCM) and H<sub>2</sub>O (DCM/H<sub>2</sub>O, 1:1), in which the enhanced performance was attributed to the good extraction capability of DCM solvent.<sup>24</sup> However, there is insufficient experimental evidence and limited understanding of critical impacts of the biphasic system on LA production using the recommended green solvents.

This study examines LA production from bread waste using PC, GVL, and isopropanol (IPA) as green co-solvent systems, i.e., PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, catalysed by dilute H<sub>2</sub>SO<sub>4</sub> to investigate how and why an efficient yield of LA could be achieved at moderate reaction conditions using these bio-derived and CO<sub>2</sub>-derived green co-solvents. Water (100%) as the greenest solvent was also evaluated as a baseline for comparison. Furthermore, this study explores the application and tuning of the binary biphasic reaction medium to intensify the concentration of the target product LA considering the potential advantages of phase separation for reactive LA 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.<sup>13</sup> 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 ( $\geq 99\%$ ) and maltose monohydrate (98%) (WAKO); levoglucosan (LG) (Fluorochem); LA (98%), and formic acid (FA) (98%) (Alfa Aesar); furfural (99%) and HMF ( $\geq 99\%$ , Sigma Aldrich); and  $\text{H}_2\text{SO}_4$  (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.<sup>13,20</sup> 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  $\text{H}_2\text{SO}_4$  were loaded in Teflon vessel and sealed, then heated to reach the desired reaction temperature (110-150°C) following a constant ramp rate ( $32^\circ\text{C min}^{-1}$ ), 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<sup>11,13</sup> and adjusted if necessary based on the

experimental observations. To substantiate the experimental results obtained in PC/H<sub>2</sub>O solvent, additional tests under the selected conditions were conducted using propylene glycol (PG) and water (PG/H<sub>2</sub>O, 1:1) for comparison.

After analysing the results obtained from different monophasic solvent systems, GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O solvents were investigated for biphasic reactions. As GVL and IPA are completely miscible in water, 30 wt%<sub>(aq)</sub> NaCl was applied as a phase modifier to prepare the biphasic system,<sup>21,25</sup> and catalytic tests were conducted following the conditions mentioned above. It is noted that the concentration of H<sub>2</sub>SO<sub>4</sub> refers to the whole solvent system (i.e., consistent for all experimental runs with different solvents, both monophasic and biphasic), whereas the concentration of NaCl refers to the reaction phase only, which is denoted as NaCl<sub>(aq)</sub>. To analyse the influence of the reaction phase and extraction phase on catalytic performance in the biphasic system, different ratios of water and organic solvent (1:1, 1:3, 3:1) were applied for the conversion. Control runs without bread waste substrate were performed for solvent systems under the selected conditions. Standard thermocouple and pressure data-logger were used during catalytic reactions to monitor and record the in-vessel reaction temperature and autogenous pressure, respectively.

### Analysis of samples

Soluble samples were obtained from each replicate, diluted with deionised water (DIW), and filtered through a membrane filter (0.45 µm) before analysis. For biphasic reactions, samples were obtained from each layer and prepared separately for analysis after dilution in DIW. High-performance liquid chromatography (HPLC) consisting of a Chromaster instrument equipped with Aminex HPX-87H column (Bio-Rad) and a refractive index detector (Hitachi, Japan) was used to analyse the soluble products; 0.01 M H<sub>2</sub>SO<sub>4</sub> was used as the mobile phase at 0.5 ml min<sup>-1</sup> flow rate at 50 °C.<sup>10,26</sup> To ensure reliable analysis, spiked samples with known concentrations of standard



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

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

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

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

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

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

## Results and discussion

### Catalytic conversion of bread waste under bio-derived and CO<sub>2</sub>-derived solvents

Facile conversion of bread waste was achieved under moderate reaction conditions, obtaining 45-72 mol% total product yield at  $130^{\circ}\text{C}$  under bio-derived and CO<sub>2</sub>-derived co-solvent systems (**Fig. 1a**). For H<sub>2</sub>O, PC/H<sub>2</sub>O, and GVL/H<sub>2</sub>O solvents, the maximum total sugars released from bread waste were 64-70 mol% in a short reaction duration of 1 min (**Fig. S1a**). In contrast, using IPA/H<sub>2</sub>O, the total sugar yield after 1 min of reaction was 43.5 mol%, increasing up to 48.8 mol% when the reaction was prolonged for 20 min. Given the total sugar yield generated at  $110^{\circ}\text{C}$  (**Fig. 1b**), hydrolysis of bread waste was faster in GVL/H<sub>2</sub>O (48.1 mol%) and PC/H<sub>2</sub>O (53.7 mol%) compared to H<sub>2</sub>O (~30 mol%) and IPA/H<sub>2</sub>O (9.4 mol%). With increasing reaction duration up to 20 min, sugar yield in H<sub>2</sub>O and IPA/H<sub>2</sub>O remained steady and generated an insignificant LA yield ~1.5 mol% after 20 min of reaction. In contrast, sugars were consumed, and LA yield increased with increasing reaction duration gradually in GVL/H<sub>2</sub>O (up to 4.8 mol%) and sharply in PC/H<sub>2</sub>O (up to 19.6 mol%) (**Fig. 1a**). <sup>13</sup>C NMR spectra of reacted solutions (1 and 20 min reaction) (**Fig. 2a**) provided further evidence for the disparity in catalytic conversion under different solvent systems. <sup>13</sup>C NMR chemical shift ( $\delta$ ) at 95.8 ppm, attributed to glucose,<sup>28</sup> was observed for all reactions. The highest intensity of glucose peak was observed for 1 min reacted solution in PC/H<sub>2</sub>O, which agrees with the maximum sugar yield measured by HPLC. In contrast, the lowest intensity of glucose peak and emerged LA peak (at 27.7, 37.6, 177 pm) along with an FA peak (at 165.45 ppm)<sup>29</sup> for 20 min reaction in PC/H<sub>2</sub>O further prove the efficient tandem catalysis in PC/H<sub>2</sub>O. The characteristic peaks for LA and FA were not detectable in IPA/H<sub>2</sub>O and H<sub>2</sub>O, while

low-intensity peaks could be observed for GVL/H<sub>2</sub>O. Besides, representative solvent peaks<sup>29</sup> were detected in the reacted solutions indicated in **Fig. 2a**.

The higher soluble product yields in PC/H<sub>2</sub>O and GVL/H<sub>2</sub>O (**Fig. 1b**) could be related to the high reactivity of the Brønsted acid catalyst due to the availability of highly active proton in the presence of aprotic co-solvents in the reaction system.<sup>13,30</sup> The extent of proton stabilisation influences the acid dissociation constant, and in water lowers the proton reactivity, which subsequently elevates the required energy level for acid-catalysed biomass conversion reactions such as hydrolysis and dehydration.<sup>30</sup> Therefore, reaction kinetics could be slower in H<sub>2</sub>O (100%) compared to a solvent system consisting of a polar aprotic solvent such as GVL and PC, which might enhance the reaction rates owing to reactive proton and facile glycosidic bond cleavage.<sup>20,31</sup> For instance, a recent study reported a ten-fold increase in reaction rate for acid-catalysed conversion of HMF to LA using GVL with 10% H<sub>2</sub>O compared to 100% H<sub>2</sub>O as solvent.<sup>32</sup> Slower conversion of bread waste was observable in the case of IPA/H<sub>2</sub>O solvent (total sugar ~10 mol%, at 110°C, 1 min) (**Fig. 1b**), where both co-solvents are protic and probably hamper the proton reactivity during conversion.

The starch contained in the bread waste substrate represents a complex structure combining linear amylose chains and highly branched amylopectin comprising  $\alpha(1\rightarrow4)$  and  $\alpha(1\rightarrow6)$  glycosidic bonds. <sup>13</sup>C NMR spectra of solid residues (**Fig. 2b**) subjected to reaction under different solvent systems (20 min) showed differences in chemical shifts than the untreated bread waste, possibly related to the changes in starch structures.<sup>33</sup> The chemical shifts observed at resonance values of 93-103, 74-85, 64-73, 55-60 ppm can be attributed to C1, C4, C2,3,5, and C6 of glucose units, respectively.<sup>11,34</sup> Resonance values attributed to C1 and C4 can be helpful to understand the 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.<sup>34-35</sup> In contrast, the resonance for C4 around 82 ppm was  
222 observed for solid residues, characteristic of an amorphous state.<sup>36</sup> 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.<sup>37-38</sup> 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  $\sim 0.51$ , 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.<sup>27</sup>

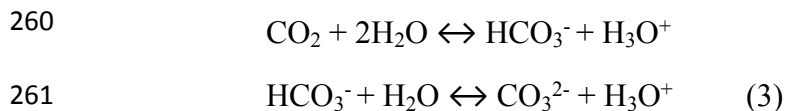
234

## LA yield enhanced by in-vessel high pressure generated in PC/H<sub>2</sub>O

Comparing different co-solvent systems, PC/H<sub>2</sub>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.<sup>9,39</sup> Under GVL/H<sub>2</sub>O solvent, sugars depleted gradually during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H<sub>2</sub>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<sub>2</sub>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<sub>2</sub>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<sub>2</sub> as reported in the literature.<sup>13,40</sup> Noticeably, ~5-15% solvent loss was recorded for reactions in PC/H<sub>2</sub>O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the reaction. Besides, <sup>13</sup>C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H<sub>2</sub>O (1 and 20 min) showed peaks at 66.4 and 67.7 ppm representing PG.<sup>29</sup> 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<sub>2</sub> pressure recorded for more prolonged reactions in PC/H<sub>2</sub>O (**Fig. 3b**).

Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from CO<sub>2</sub> generation during catalytic conversion in PC/H<sub>2</sub>O might enhance the LA production rate. Another influential factor could be the increased acidity due to carbonic acid derived from partial

dissolution of CO<sub>2</sub> during the reaction, which might enhance sugar dehydration.<sup>41</sup> Solution acidity can arise through *in situ* formation and dissociation of carbonic acid, as given in Eq. (3).<sup>42</sup>



The acidity (pH) associated with CO<sub>2</sub> generated during 3-20 min reaction in PC/H<sub>2</sub>O was estimated, following the scheme reported in the literature.<sup>43-44</sup> The estimated CO<sub>2</sub>-derived pH value for specified reaction conditions was ~3.5, i.e., considerably higher than the H<sub>2</sub>SO<sub>4</sub> derived pH (~0.5) in this study. Therefore, CO<sub>2</sub>-derived pH on its own might not be sufficient to catalyse tandem reactions and significantly enhance LA yield. In other words, LA yield might be improved probably by PC/H<sub>2</sub>O generated CO<sub>2</sub> pressure more than CO<sub>2</sub>-derived acidity during the catalytic conversion of bread waste. To testify this postulation, an additional test using PC/H<sub>2</sub>O was conducted, in which autogenous pressure developed due to PC degradation (~22 bar) was released after 5 min reaction, and then the solution underwent reaction for another 15 min (**Fig. 3c**). Compared to continuous 20 min reaction in PC/H<sub>2</sub>O (LA yield 19.6 mol%), only about half of LA was produced (LA yield 11.2 mol%) when the pressure was released prematurely during the reaction. After the pressure release, the autogenous pressure was ~4.2 bar from the beginning till the end point of additional 15-min reaction. Moreover, supplementary tests using PG/H<sub>2</sub>O only generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA yield obtained in PC/H<sub>2</sub>O, therefore disproving any favourable influences by PG solvent (decomposed from PC) on the catalytic performance. These experimental evidences confirm the crucial enhancement of reaction pressure on the catalytic LA production.

## Intensification of LA yield through phase separation

Among co-solvent systems, PC/H<sub>2</sub>O 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<sub>2</sub>O and IPA/H<sub>2</sub>O (**Fig. 1a**), which could be further converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O, 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<sub>2</sub>O (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<sub>2</sub>O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than GVL/H<sub>2</sub>O system, corroborating the positive role of aprotic GVL solvent in enhancing proton reactivity for less energy-intensive tandem catalysis.<sup>10,30</sup>

The biphasic solvent systems (prepared using 30 wt% NaCl<sub>(aq)</sub>) 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<sub>2</sub>O and IPA/H<sub>2</sub>O 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<sub>2</sub>O and IPA/H<sub>2</sub>O. While biphasic GVL/H<sub>2</sub>O selectively generated LA as the main product 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H<sub>2</sub>O 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<sub>2</sub>O indicated that the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely

recommended solvent for HMF production, IPA can create a shielding effect around HMF that helps to prevent its rehydration and suppress further conversion to byproducts such as insoluble humins.<sup>45-46</sup> A recent study revealed that the rate constant for fructose to HMF was considerably higher than that of HMF to degradation products when IPA was present in the solvent system,<sup>46</sup> echoing the experimental observations in this study where low LA selectivity was obtained in IPA/H<sub>2</sub>O solvent system. In other words, IPA/H<sub>2</sub>O could be considered as a potential solvent for HMF production in future investigations. By contrast, in the presence of GVL solvent, H<sub>2</sub>SO<sub>4</sub> catalysed HMF production could be rapid and readily converted to LA at high acid strength.<sup>47</sup> Considerable LA yield achieved in biphasic GVL/H<sub>2</sub>O in this study (26.8 mol%, at 150°C, 20 min) proves the high efficiency of H<sub>2</sub>SO<sub>4</sub>/GVL/H<sub>2</sub>O system for LA production.

As GVL/H<sub>2</sub>O biphasic solvent was the most efficient for intensifying LA yield at moderate conditions, a comprehensive investigation was conducted for bread waste conversion in the co-solvent system following varied reaction conditions (150°C, 10-20 min). In biphasic GVL/H<sub>2</sub>O, LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H<sub>2</sub>O, 1:1) (**Fig. 5a**). However, a slight decrease in LA yield was observed after 20 min, suggesting that LA started to degrade with prolonged reaction. The major product in monophasic GVL/H<sub>2</sub>O (1:1, 15 min) was glucose (34.6 mol%), while the biphasic system selectively generated LA (~28 mol%) as the major product. The LA yield increased up to ~2.5 times in the biphasic system compared to the monophasic one (~11 mol%) (150°C, 15 min), implying that phase separation could be beneficial for intensive LA production and upscaling to industrial scale.

Essentially, to develop an efficient biphasic reaction medium, it is necessary to understand the contribution and influences of the reaction phase (H<sub>2</sub>O) and the extraction phase (GVL) to optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H<sub>2</sub>O



biphasic system, catalytic tests were conducted with various ratios of GVL and H<sub>2</sub>O (1:1, 1:3, and 3:1 of GVL/H<sub>2</sub>O). The partition coefficient for LA ( $R_{LA}$ ) in the GVL/H<sub>2</sub>O biphasic solvent was calculated to evaluate the effect of the extraction phase (GVL) in the system. The  $R_{LA}$  achieved for 10-15 min reaction was 4.2 when 1:1 GVL/H<sub>2</sub>O was applied for reaction (**Fig. 5b**), indicating a higher distribution of LA in the organic phase compared to the aqueous phase. Therefore, GVL solvent can be considered highly effective for reactive LA extraction. The partitioning of LA obtained in this study ( $R_{LA}$  4.2) is comparable to a previous study that reported  $R_{LA}$  ranging 3.7-4 using cellulose as feedstock.<sup>21</sup>

The total yield of LA increased (27.4-32 mol%) when a higher fraction of H<sub>2</sub>O (1:3, GVL/H<sub>2</sub>O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-17.1 mol%) when a lower fraction of H<sub>2</sub>O (3:1, GVL/H<sub>2</sub>O) was applied (**Fig. 5b**). Though the total LA yield increased with a higher fraction of H<sub>2</sub>O, the extraction of LA was found to be inefficient. The partition coefficient achieved was only 1.1 (1:3, GVL/H<sub>2</sub>O), indicating nearly even distribution of produced LA in the reaction and extraction phases due to the lower fraction of GVL applied. In comparison, ~97% of the total LA produced was extracted into the GVL phase when a higher fraction of GVL (3:1, GVL/H<sub>2</sub>O) was applied for reaction. However, a considerable decrease in total LA yield was observed, possibly due to the lack of sufficient aqueous phase available for reaction. These observations suggested the indispensable contribution of both reaction and extraction phases for an efficient biphasic system for LA production. Considering LA yield (27.4 mol%) and  $R_{LA}$  (4.2), the 1:1 GVL/H<sub>2</sub>O biphasic system (150°C, 15 min) provided the best performance for intensive LA production.

To reflect further on the mechanism and roles of catalytic species in NaCl modified GVL/H<sub>2</sub>O biphasic system, additional tests were performed under the selected reaction conditions.

In the case of reaction conducted with only NaCl (30 wt%) without acid catalyst, only marginal product yield was observed (**Fig. 6a**). When NaCl was applied together with H<sub>2</sub>SO<sub>4</sub> for bread waste conversion, an increase in LA yield was observed compared to the reaction in the presence of H<sub>2</sub>SO<sub>4</sub> without salt addition. These observations indicate that NaCl alone could not catalyse the desired reaction yet it may act synergistically with H<sub>2</sub>SO<sub>4</sub> enhancing the LA production in the aqueous phase during biphasic conversion of bread waste. Product distributions in the aqueous and GVL phases in the specified reaction conditions are provided in **Fig. S3**. The synergistic catalysis by NaCl and H<sub>2</sub>SO<sub>4</sub> together with simultaneous efficient extraction of LA into GVL could account for the high LA yield obtained in the GVL/H<sub>2</sub>O biphasic system.

Moreover, the recyclability of the aqueous phase containing H<sub>2</sub>SO<sub>4</sub> was investigated. After the catalytic run (reaction and cooling), the reacted organic phase was removed and fresh GVL and bread waste substrate were applied for another cycle of catalytic reaction (run-2) again while retaining the aqueous phase from the previous run without adding extra H<sub>2</sub>SO<sub>4</sub>. Similarly, the third cycle of catalytic reaction (run-3) was conducted. In the 2<sup>nd</sup> and 3<sup>rd</sup> run (**Fig. 6b**), 15 mol% and 13 mol% LA was obtained, respectively, compared to the LA yield (28 mol%) obtained in the initial run, which suggested that the acid catalyst could be retained in the aqueous phase and recycled for further conversion, though a certain degree of decrease in LA yield was observed. Future studies would be required for evaluating the biphasic system in a continuous reaction mode, which may be more efficient compared to the batch reaction mode.

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

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

### Perspectives on LA production and solvent recycling

To evaluate the efficiency of the catalytic system for LA production, LA yield relative to theoretical LA yield of bread waste substrate (considering total available carbohydrate and possible maximum theoretical yield (64.5%)) was calculated and compared with the reported achievements with commercially available starch substrates in the existing literature (**Table 1**). For PC/H<sub>2</sub>O (130°C, 20 min) and GVL/H<sub>2</sub>O biphasic solvents (150°C, 15 min), 45.7% and 66% LA yield was achieved relative to theoretical yield, respectively. This is considered promising in comparison to the reported LA yield (45.6-66.4%) from commercially available starch substrates in previous studies<sup>49-50</sup> where the conversion was conducted using comparatively harsh reaction conditions. For other recent studies where no direct comparison is possible due to the lack of data regarding relative LA yield,<sup>17,51</sup> it should be noted that much longer reaction duration was required to obtain the reported LA yield.

The recyclability of GVL/H<sub>2</sub>O biphasic solvent was investigated and discussed in the previous section. For PC/H<sub>2</sub>O solvent, despite partial decomposition of PC during acid catalysis, it offers various advantages as a solvent because a high product yield can be obtained with a moderate temperature and a short duration, which play a critical role in reducing the energy

consumption and reactor size. The production of PC from CO<sub>2</sub> is beneficial for process economy and environmental sustainability in terms of CO<sub>2</sub> utilisation. In the application of PC solvent, the derived CO<sub>2</sub> after reaction can be captured and recycled for PC production or other CO<sub>2</sub> based biorefineries, which are conducive to fostering the circular economy. The spent organic solvents can be recycled after separation and purification following commonly used techniques such as fractional distillation. For instance, a comprehensive life cycle assessment (LCA) on solvent waste recovery<sup>52</sup> demonstrated that implementing a solvent recovery system can reduce the environmental footprint of the total solvent manufacturing, usage, and disposal process. The energy requirements and emissions associated with the solvent recovery process have been recognised to be trivial in comparison to the emissions due to virgin solvent production and spent solvent disposal by incineration.

## Conclusions

This study provides comprehensive insights into the critical factors for intensive LA production, which can be conducive to the technology scale-up. The bio-derived and CO<sub>2</sub>-derived co-solvents in this study, i.e., PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, could facilitate H<sub>2</sub>SO<sub>4</sub> catalysed tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency. PC/H<sub>2</sub>O solvent was the most efficient for LA production using moderate reaction conditions, which could be attributed to the CO<sub>2</sub> pressure generated *in situ* through solvent (PC) degradation. Besides, catalytic performance could be significantly enhanced in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O using the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the final concentration of LA. GVL/H<sub>2</sub>O biphasic solvent seems promising considering LA yield (28 mol%) and LA partitioning ( $R_{LA}$  4.2) achieved in the study. The bio-derived and CO<sub>2</sub>-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

## 425 **Acknowledgements**

426 The authors appreciate the financial support from the Hong Kong International Airport  
427 Environmental Fund (Phase 2) and Hong Kong Research Grants Council (PolyU 15222020). The  
428 authors also acknowledge the support of the University Research Facility on Chemical and  
429 Environmental Analysis (UCEA) of PolyU.

430 **References**

- 431 (1) UNEP. Food Waste Index Report 2021 [http://www.unep.org/resources/report/unep-food-](http://www.unep.org/resources/report/unep-food-waste-index-report-2021)  
432 [waste-index-report-2021](http://www.unep.org/resources/report/unep-food-waste-index-report-2021) (accessed Apr 14, 2021).
- 433 (2) Xiong, X.; Yu, I. K. M.; Tsang, D. C. W.; Bolan, N. S.; Ok, Y. S.; Igalavithana, A. D.;  
434 Kirkham, M. B.; Kim, K.-H.; Vikrant, K. Value-Added Chemicals from Food Supply  
435 Chain Wastes: State-of-the-Art Review and Future Prospects. *Chem. Eng. J.* **2019**, *375*,  
436 121983. DOI:10.1016/j.cej.2019.121983
- 437 (3) Mak, T. M. W.; Xiong, X.; Tsang, D. C. W.; Yu, I. K. M.; Poon, C. S. Sustainable Food  
438 Waste Management towards Circular Bioeconomy: Policy Review, Limitations and  
439 Opportunities. *Bioresour. Technol.* **2020**, *297*, 122497.  
440 DOI:10.1016/j.biortech.2019.122497.
- 441 (4) Chen, S. S.; Maneerung, T.; Tsang, D. C. W.; Ok, Y. S.; Wang, C.-H. Valorization of  
442 Biomass to Hydroxymethylfurfural, Levulinic Acid, and Fatty Acid Methyl Ester by  
443 Heterogeneous Catalysts. *Chem. Eng. J.* **2017**, *328*, 246–273.  
444 DOI:10.1016/j.cej.2017.07.020.
- 445 (5) Hayes, G. C.; Becer, C. R. Levulinic Acid: A Sustainable Platform Chemical for Novel  
446 Polymer Architectures. *Polym. Chem.* **2020**, *11*, 4068–4077. DOI:10.1039/D0PY00705F.
- 447 (6) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Ng, Y. H.; Ok, Y. S.; Sherwood, J.; Clark, J. H.  
448 Green Synthesis of Gamma-Valerolactone (GVL) through Hydrogenation of Biomass-  
449 Derived Levulinic Acid Using Non-Noble Metal Catalysts: A Critical Review. *Chem. Eng.*  
450 *J.* **2019**, *372*, 992–1006. DOI:10.1016/j.cej.2019.04.199.
- 451 (7) Antonetti, C.; Licursi, D.; Fulignati, S.; Valentini, G.; Raspolli Galletti, A. New Frontiers  
452 in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as  
453 Starting Feedstock. *Catalysts* **2016**, *6*, 196. DOI:10.3390/catal6120196.
- 454 (8) Pileidis, F. D.; Titirici, M.-M. Levulinic Acid Biorefineries: New Challenges for Efficient  
455 Utilization of Biomass. *ChemSusChem* **2016**, *9*, 562–582. DOI:10.1002/cssc.201501405.
- 456 (9) Chen, S. S.; Yu, I. K. M.; Tsang, D. C. W.; Yip, A. C. K.; Khan, E.; Wang, L.; Ok, Y. S.;  
457 Poon, C. S. Valorization of Cellulosic Food Waste into Levulinic Acid synthesized by  
458 Heterogeneous Brønsted Acids: Temperature and Solvent Effects. *Chem. Eng. J.* **2017**,  
459 *327*, 328–335. DOI:10.1016/j.cej.2017.06.108
- 460 (10) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Su, Z.; Hu, C.; Wu, K. C. W.; Yip, A. C. K.; Ok,  
461 Y. S.; Poon, C. S. Influence of Green Solvent on Levulinic Acid Production from  
462 Lignocellulosic Paper Waste. *Bioresour. Technol.* **2020**, *298*, 122544.  
463 DOI:10.1016/j.biortech.2019.122544.
- 464 (11) Yu, I. K. M.; Fan, J.; Budarin, V. L.; Bouxin, F. P.; Clark, J. H.; Tsang, D. C. W. NaCl-  
465 Promoted Phase Transition and Glycosidic Bond Cleavage under Microwave Heating for  
466 Energy-Efficient Biorefinery of Rice Starch. *Green Chem.* **2020**, *22*, 7355–7365.  
467 DOI:10.1039/D0GC01761B.
- 468 (12) Yu, I. K. M.; Tsang, D. C. W.; Chen, S. S.; Wang, L.; Hunt, A. J.; Sherwood, J.; De  
469 Oliveira Vigier, K.; Jérôme, F.; Ok, Y. S.; Poon, C. S. Polar Aprotic Solvent-Water  
470 Mixture as the Medium for Catalytic Production of Hydroxymethylfurfural (HMF) from  
471 Bread Waste. *Bioresour. Technol.* **2017**, *245*, 456–462.  
472 DOI:10.1016/j.biortech.2017.08.170.
- 473 (13) Yu, I. K. M.; Tsang, D. C. W.; Yip, A. C. K.; Hunt, A. J.; Sherwood, J.; Shang, J.; Song,  
474 H.; Ok, Y. S.; Poon, C. S. Propylene Carbonate and  $\gamma$ -Valerolactone as Green Solvents

- Enhance Sn(IV)-Catalysed Hydroxymethylfurfural (HMF) Production from Bread Waste. *Green Chem.* **2018**, *20*, 2064–2074. DOI:10.1039/C8GC00358K.
- (14) Antonetti, C.; Licursi, D.; Raspolli Galletti, A. M. New Intensification Strategies for the Direct Conversion of Real Biomass into Platform and Fine Chemicals: What Are the Main Improvable Key Aspects? *Catalysts* **2020**, *10*, 961. DOI:10.3390/catal10090961.
- (15) Chen, S. S.; Wang, L.; Yu, I. K. M.; Tsang, D. C. W.; Hunt, A. J.; Jérôme, F.; Zhang, S.; Ok, Y. S.; Poon, C. S. Valorization of Lignocellulosic Fibres of Paper Waste into Levulinic Acid Using Solid and Aqueous Brønsted Acid. *Bioresour. Technol.* **2018**, *247*, 387–394. DOI:10.1016/j.biortech.2017.09.110.
- (16) Dyson, P. J.; Jessop, P. G. Solvent Effects in Catalysis: Rational Improvements of Catalysts via Manipulation of Solvent Interactions. *Catal. Sci. Technol.* **2016**, *6*, 3302–3316. DOI:10.1039/C5CY02197A.
- (17) Lui, M. Y.; Wong, C. Y. Y.; Choi, A. W.-T.; Mui, Y. F.; Qi, L.; Horváth, I. T. Valorization of Carbohydrates of Agricultural Residues and Food Wastes: A Key Strategy for Carbon Conservation. *ACS Sustain. Chem. Eng.* **2019**, *7*, 17799–17807. DOI:10.1021/acssuschemeng.9b04242.
- (18) Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C. R.; Abou-Shehadeh, S.; Dunn, P. J. CHEM21 Selection Guide of Classical- and Less Classical-Solvents. *Green Chem.* **2016**, *18*, 288–296. DOI:10.1039/C5GC01008J.
- (19) Gao, F.; Bai, R.; Ferlin, F.; Vaccaro, L.; Li, M.; Gu, Y. Replacement Strategies for Non-Green Dipolar Aprotic Solvents. *Green Chem.* **2020**, *22*, 6240–6257. DOI:10.1039/D0GC02149K.
- (20) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Fan, J.; Clark, J. H.; Jiang, Z.; Su, Z.; Hu, C.; Poon, C. S. Efficient Depolymerization of Cellulosic Paper Towel Waste Using Organic Carbonate Solvents. *ACS Sustain. Chem. Eng.* **2020**, *8*, 13100–13110. DOI:10.1021/acssuschemeng.0c04102.
- (21) Wettstein, S. G.; Alonso, D. M.; Chong, Y.; Dumesic, J. A. Production of Levulinic Acid and Gamma-Valerolactone (GVL) from Cellulose Using GVL as a Solvent in Biphasic Systems. *Energy Environ. Sci.* **2012**, *5*, 8199. DOI:10.1039/c2ee22111j.
- (22) Wang, J.; Cui, H.; Wang, Y.; Zhao, R.; Xie, Y.; Wang, M.; Yi, W. Efficient Catalytic Conversion of Cellulose to Levulinic Acid in the Biphasic System of Molten Salt Hydrate and Methyl Isobutyl Ketone. *Green Chem.* **2020**, *22*, 4240–4251. DOI:10.1039/D0GC00897D.
- (23) Rihko-Struckmann, L. K.; Oluyinka, O.; Sahni, A.; McBride, K.; Fachet, M.; Ludwig, K.; Sundmacher, K. Transformation of Remnant Algal Biomass to 5-HMF and Levulinic Acid: Influence of a Biphasic Solvent System. *RSC Adv.* **2020**, *10*, 24753–24763. DOI:10.1039/D0RA02784G.
- (24) Kumar, S.; Ahluwalia, V.; Kundu, P.; Sangwan, R. S.; Kansal, S. K.; Runge, T. M.; Elumalai, S. Improved Levulinic Acid Production from Agri-Residue Biomass in Biphasic Solvent System through Synergistic Catalytic Effect of Acid and Products. *Bioresour. Technol.* **2018**, *251*, 143–150. DOI:10.1016/j.biortech.2017.12.033.
- (25) Jiang, Z.; Remón, J.; Li, T.; Budarin, V. L.; Fan, J.; Hu, C.; Clark, J. H. A One-Pot Microwave-Assisted NaCl–H<sub>2</sub>O/GVL Solvent System for Cellulose Conversion to 5-Hydroxymethylfurfural and Saccharides with in Situ Separation of the Products. *Cellulose* **2019**, *26*, 8383–8400. DOI:10.1007/s10570-019-02362-8.

- (26) Yu, I. K. M.; Xiong, X.; Tsang, D. C. W.; Ng, Y. H.; Clark, J. H.; Fan, J.; Zhang, S.; Hu, C.; Ok, Y. S. Graphite Oxide- and Graphene Oxide-Supported Catalysts for Microwave-Assisted Glucose Isomerisation in Water. *Green Chem.* **2019**, *21*, 4341–4353. DOI:10.1039/C9GC00734B.
- (27) Foresti, M. L.; Williams, M. del P.; Martínez-García, R.; Vázquez, A. Analysis of a Preferential Action of  $\alpha$ -Amylase from *B. Licheniformis* towards Amorphous Regions of Waxy Maize Starch. *Carbohydr. Polym.* **2014**, *102*, 80–87. DOI:10.1016/j.carbpol.2013.11.013.
- (28) Qi, L.; Alamillo, R.; Elliott, W. A.; Andersen, A.; Hoyt, D. W.; Walter, E. D.; Han, K. S.; Washton, N. M.; Rioux, R. M.; Dumesic, J. A.; Scott, S. L. Operando Solid-State NMR Observation of Solvent-Mediated Adsorption-Reaction of Carbohydrates in Zeolites. *ACS Catal.* **2017**, *7*, 3489–3500. DOI:10.1021/acscatal.7b01045.
- (29) AIST. Spectral Database for Organic Compounds (SDBS). **2018**, [https://sdb.sdb.aist.go.jp/sdb/cgi-bin/cre\\_index.cgi](https://sdb.sdb.aist.go.jp/sdb/cgi-bin/cre_index.cgi) (accessed May 10, 2021).
- (30) Mellmer, M. A.; Sener, C.; Gallo, J. M. R.; Luterbacher, J. S.; Alonso, D. M.; Dumesic, J. A. Solvent Effects in Acid-Catalyzed Biomass Conversion Reactions. *Angew. Chem. Int. Ed.* **2014**, *53*, 11872–11875. DOI:10.1002/anie.201408359.
- (31) Mellmer, M. A.; Alonso, D. M.; Luterbacher, J. S.; Gallo, J. M. R.; Dumesic, J. A. Effects of  $\gamma$ -Valerolactone in Hydrolysis of Lignocellulosic Biomass to Monosaccharides. *Green Chem.* **2014**, *16*, 4659–4662. DOI:10.1039/C4GC01768D.
- (32) Mellmer, M. A.; Sanpitakserree, C.; Demir, B.; Bai, P.; Ma, K.; Neurock, M.; Dumesic, J. A. Solvent-Enabled Control of Reactivity for Liquid-Phase Reactions of Biomass-Derived Compounds. *Nat. Catal.* **2018**, *1* (3), 199–207. DOI:10.1038/s41929-018-0027-3.
- (33) Flanagan, B. M.; Gidley, M. J.; Warren, F. J. Rapid Quantification of Starch Molecular Order through Multivariate Modelling of  $^{13}\text{C}$  CP/MAS NMR Spectra. *Chem. Commun.* **2015**, *51*, 14856–14858. DOI:10.1039/C5CC06144J.
- (34) Cai, J.; Cai, C.; Man, J.; Yang, Y.; Zhang, F.; Wei, C. Crystalline and Structural Properties of Acid-Modified Lotus Rhizome C-Type Starch. *Carbohydr. Polym.* **2014**, *102*, 799–807. DOI:10.1016/j.carbpol.2013.10.088.
- (35) Atichokudomchai, N.; Varavinit, S.; Chinachoti, P. A Study of Ordered Structure in Acid-Modified Tapioca Starch by C CP/MAS Solid-State NMR. *Carbohydr. Polym.* **2004**, *58*, 383–389. DOI:10.1016/j.carbpol.2004.07.017.
- (36) Mutungi, C.; Passauer, L.; Onyango, C.; Jaros, D.; Rohm, H. Debranched Cassava Starch Crystallinity Determination by Raman Spectroscopy: Correlation of Features in Raman Spectra with X-Ray Diffraction and  $^{13}\text{C}$  CP/MAS NMR Spectroscopy. *Carbohydr. Polym.* **2012**, *87*, 598–606. DOI:10.1016/j.carbpol.2011.08.032.
- (37) Morrison, W. R.; Tester, R. F.; Gidley, M. J.; Karkalas, J. Resistance to Acid Hydrolysis of Lipid-Complexed Amylose and Lipid-Free Amylose in Lintnerised Waxy and Non-Waxy Barley Starches. *Carbohydr. Res.* **1993**, *245*, 289–302. DOI:10.1016/0008-6215(93)80078-S.
- (38) Hoover, R. Acid-treated Starches. *Food Rev. Int.* **2000**, *16*, 369–392. DOI: 10.1081/FRI-100100292.
- (39) Lappalainen, K.; Vogeler, N.; Kärkkäinen, J.; Dong, Y.; Niemelä, M.; Rusanen, A.; Ruotsalainen, A. L.; Wäli, P.; Markkola, A.; Lassi, U. Microwave-Assisted Conversion of Novel Biomass Materials into Levulinic Acid. *Biomass Convers. Biorefinery* **2018**, *8*, 965–970. DOI:10.1007/s13399-018-0334-6.



- (40) Zhang, Z.; O'Hara, I. M.; Rackemann, D. W.; Doherty, W. O. S. Low Temperature Pretreatment of Sugarcane Bagasse at Atmospheric Pressure Using Mixtures of Ethylene Carbonate and Ethylene Glycol. *Green Chem* **2013**, *15*, 255–264. DOI:10.1039/C2GC36323B.
- (41) Morais, A. R. C.; Matuchaki, M. D. D. J.; Andreus, J.; Bogel-Lukasik, R. A Green and Efficient Approach to Selective Conversion of Xylose and Biomass Hemicellulose into Furfural in Aqueous Media Using High-Pressure CO<sub>2</sub> as a Sustainable Catalyst. *Green Chem.* **2016**, *18*, 2985–2994. DOI:10.1039/C6GC00043F.
- (42) Jing, S.; Cao, X.; Zhong, L.; Peng, X.; Zhang, X.; Wang, S.; Sun, R. In Situ Carbonic Acid from CO<sub>2</sub>: A Green Acid for Highly Effective Conversion of Cellulose in the Presence of Lewis Acid. *ACS Sustain. Chem. Eng.* **2016**, *4*, 4146–4155. DOI:10.1021/acssuschemeng.6b00623.
- (43) Van Walsum, G. P. Severity Function Describing the Hydrolysis of Xylan Using Carbonic Acid. In *Twenty-Second Symposium on Biotechnology for Fuels and Chemicals*; Davison, B. H., McMillan, J., Finkelstein, M., Eds.; ABAB Symposium; Humana Press: Totowa, NJ, **2001**, DOI:10.1007/978-1-4612-0217-2\_27.
- (44) Toscan, A.; Morais, A. R. C.; Paixão, S. M.; Alves, L.; Andreus, J.; Camassola, M.; Dillon, A. J. P.; Lukasik, R. M. High-Pressure Carbon Dioxide/Water Pre-Treatment of Sugarcane Bagasse and Elephant Grass: Assessment of the Effect of Biomass Composition on Process Efficiency. *Bioresour. Technol.* **2017**, *224*, 639–647. DOI:10.1016/j.biortech.2016.11.101.
- (45) Mushrif, S. H.; Caratzoulas, S.; Vlachos, D. G. Understanding Solvent Effects in the Selective Conversion of Fructose to 5-Hydroxymethyl-Furfural: A Molecular Dynamics Investigation. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2637. DOI:10.1039/c2cp22694d.
- (46) Agutaya, J. K. C. N.; Inoue, R.; Vin Tsie, S. S.; Quitain, A. T.; de la Peña-García, J.; Pérez-Sánchez, H.; Sasaki, M.; Kida, T. Metal-Free Synthesis of HMF from Glucose Using the Supercritical CO<sub>2</sub>–Subcritical H<sub>2</sub>O–Isopropanol System. *Ind. Eng. Chem. Res.* **2020**, *59*, 16527–16538. DOI:10.1021/acs.iecr.0c03551.
- (47) Qi, L.; Mui, Y. F.; Lo, S. W.; Lui, M. Y.; Akien, G. R.; Horváth, I. T. Catalytic Conversion of Fructose, Glucose, and Sucrose to 5-(Hydroxymethyl)Furfural and Levulinic and Formic Acids in  $\gamma$ -Valerolactone As a Green Solvent. *ACS Catal.* **2014**, *4*, 1470–1477. DOI:10.1021/cs401160y.
- (48) Flannelly, T.; Lopes, M.; Kupiainen, L.; Dooley, S.; Leahy, J. J. Non-Stoichiometric Formation of Formic and Levulinic Acids from the Hydrolysis of Biomass Derived Hexose Carbohydrates. *RSC Adv.* **2016**, *6*, 5797–5804. DOI:10.1039/C5RA25172A.
- (49) Fang, Q.; Hanna, M. A. Experimental Studies for Levulinic Acid Production from Whole Kernel Grain Sorghum. *Bioresour. Technol.* **2002**, *81*, 187–192. DOI:10.1016/S0960-8524(01)00144-4.
- (50) Cha, J. Y.; Hanna, M. A. Levulinic Acid Production Based on Extrusion and Pressurized Batch Reaction. *Ind. Crops Prod.* **2002**, *16*, 109–118. DOI:10.1016/S0926-6690(02)00033-X.
- (51) Vyver, S. V. de; Thomas, J.; Geboers, J.; Keyzer, S.; Smet, M.; Dehaen, W.; A. Jacobs, P.; F. Sels, B. Catalytic Production of Levulinic Acid from Cellulose and Other Biomass-Derived Carbohydrates with Sulfonated Hyperbranched Poly(Arylene Oxindole)s. *Energy Environ. Sci.* **2011**, *4*, 3601–3610. DOI:10.1039/C1EE01418H.

- 611 (52) Raymond, M. J.; Slater, C. S.; Savelski, M. J. LCA Approach to the Analysis of Solvent  
612 Waste Issues in the Pharmaceutical Industry. *Green Chem.* **2010**, *12*, 1826–1834.  
613 DOI:10.1039/C003666H.  
614

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

Shanta Dutta <sup>a</sup>, Iris K.M. Yu <sup>a,b</sup>, Jiajun Fan <sup>c</sup>, James H. Clark <sup>c</sup>, and Daniel C.W. Tsang <sup>a,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

<sup>b</sup> Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany.

<sup>c</sup> Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK.

\*Corresponding author, [dan.tsang@polyu.edu.hk](mailto: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<sub>2</sub>-derived green co-solvents for LA synthesis. In-vessel pressure generated in PC/H<sub>2</sub>O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O. In PC/H<sub>2</sub>O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H<sub>2</sub>SO<sub>4</sub>), 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<sub>2</sub>O through phase separation using NaCl (30 wt%<sub>(aq)</sub>). 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<sub>2</sub>O (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<sub>2</sub>O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H<sub>2</sub>O 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.<sup>1</sup> Such an enormous  
43 amount of food waste requires proper handling to minimise pollution risks and be diverted from  
44 landfill disposal.<sup>2</sup> 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.<sup>3</sup>

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.<sup>4-5</sup>  
49 Besides, LA serves as a building block for the production of various value-added derivatives such  
50 as gamma-valerolactone (GVL),<sup>6</sup> succinic acid, diphenolic acid,<sup>7-8</sup> alkyl levulinates, 2-methyl-  
51 tetrahydrofuran, etc.<sup>5</sup> Considering the low cost and high catalytic activity for tandem hydrolysis  
52 and dehydration reactions, mineral acids such as H<sub>2</sub>SO<sub>4</sub> and HCl are generally used for LA  
53 production from diverse biomass feedstock including food waste, paper waste, etc.<sup>9-10</sup> Starch-rich  
54 foods such as rice, bread, and potatoes are commonly consumed and constitute a significant  
55 proportion of global food waste,<sup>11</sup> 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.<sup>12-13</sup> In this study, bread waste serves as the representative starch-rich feedstock  
59 for the catalytic production of LA.

Appropriate reaction conditions and solvent selection are critical for selective and cost-effective LA production.<sup>14</sup> As the greenest and environmentally benign solvent, water has been used as a reaction medium for LA synthesis. However, harsh reaction conditions, i.e., high temperature and acidity, are required when using water as the reaction medium resulting in an energy-intensive process and high byproduct (humin) formation.<sup>15</sup> The selection of a suitable solvent is necessary, as it not only serves as a reaction medium, but also influences the catalytic process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the byproduct formation, etc.<sup>13,16</sup> Owing to the need for selective and high-efficiency chemical synthesis, various organic solvents as reaction medium have been widely investigated, such as dimethylsulfoxide (DMSO),<sup>9</sup> tetrahydrofuran (THF), dimethylformamide (DMF),<sup>7</sup> GVL, acetone, etc.<sup>10,17</sup> However, conventional organic solvents DMSO, DMF, THF, etc., are widely considered “non-green” due to their direct or indirect detrimental effects on the natural environment and human health and safety. Therefore, the use of alternative “green” solvents, and especially those which are renewable and bio-derived (GVL, alcohols, etc.) or CO<sub>2</sub>-derived (propylene carbonate (PC), dimethyl carbonate (DMC), etc.), are recommended for future applications.<sup>18-19</sup> Furthermore, enhanced catalytic conversion of biowaste using these bio-derived and CO<sub>2</sub>-derived solvents was reported in recent studies,<sup>10,13,20</sup> yet their influences should be evaluated in comparable conditions to validate their efficiency and elucidate the critical factors for catalytic LA production.

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

be using the biphasic solvent system comprising two immiscible layers. The aqueous layer contains the acid catalyst and serves as the reactive phase, while the organic layer acts as the extractive phase, facilitating simultaneous production and extraction of LA, which might enhance LA yield and selectivity.<sup>21-22</sup> For instance, a recent study on the conversion of remnant algal biomass reported a significant enhancement of hydroxymethylfurfural (HMF) and LA yield using acidic ZSM-5 zeolite as a heterogeneous catalyst when utilising a biphasic solvent system composed of methyl isobutyl ketone (MIBK) and H<sub>2</sub>O with NaCl as the phase modifier.<sup>23</sup> Another study achieved a ~4 fold increase in LA yield from rice straw using a biphasic reaction medium containing dichloromethane (DCM) and H<sub>2</sub>O (DCM/H<sub>2</sub>O, 1:1), in which the enhanced performance was attributed to the good extraction capability of DCM solvent.<sup>24</sup> However, there is insufficient experimental evidence and limited understanding of critical impacts of the biphasic system on LA production using the recommended green solvents.

This study examines LA production from bread waste using PC, GVL, and isopropanol (IPA) as green co-solvent systems, i.e., PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, catalysed by dilute H<sub>2</sub>SO<sub>4</sub> to investigate how and why an efficient yield of LA could be achieved at moderate reaction conditions using these bio-derived and CO<sub>2</sub>-derived green co-solvents. Water (100%) as the greenest solvent was also evaluated as a baseline for comparison. Furthermore, this study explores the application and tuning of the binary biphasic reaction medium to intensify the concentration of the target product LA considering the potential advantages of phase separation for reactive LA 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.<sup>13</sup> 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  $\text{H}_2\text{SO}_4$  (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.<sup>13,20</sup> 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  $\text{H}_2\text{SO}_4$  were  
121 loaded in Teflon vessel and sealed, then heated to reach the desired reaction temperature (110-  
122  $150^\circ\text{C}$ ) following a constant ramp rate ( $32^\circ\text{C min}^{-1}$ ), 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<sup>11,13</sup> and adjusted if necessary based on the



experimental observations. To substantiate the experimental results obtained in PC/H<sub>2</sub>O solvent, additional tests under the selected conditions were conducted using propylene glycol (PG) and water (PG/H<sub>2</sub>O, 1:1) for comparison.

After analysing the results obtained from different monophasic solvent systems, GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O solvents were investigated for biphasic reactions. As GVL and IPA are completely miscible in water, 30 wt%<sub>(aq)</sub> NaCl was applied as a phase modifier to prepare the biphasic system,<sup>21,25</sup> and catalytic tests were conducted following the conditions mentioned above. It is noted that the concentration of H<sub>2</sub>SO<sub>4</sub> refers to the whole solvent system (i.e., consistent for all experimental runs with different solvents, both monophasic and biphasic), whereas the concentration of NaCl refers to the reaction phase only, which is denoted as NaCl<sub>(aq)</sub>. To analyse the influence of the reaction phase and extraction phase on catalytic performance in the biphasic system, different ratios of water and organic solvent (1:1, 1:3, 3:1) were applied for the conversion. Control runs without bread waste substrate were performed for solvent systems under the selected conditions. Standard thermocouple and pressure data-logger were used during catalytic reactions to monitor and record the in-vessel reaction temperature and autogenous pressure, respectively.

### Analysis of samples

Soluble samples were obtained from each replicate, diluted with deionised water (DIW), and filtered through a membrane filter (0.45 µm) before analysis. For biphasic reactions, samples were obtained from each layer and prepared separately for analysis after dilution in DIW. High-performance liquid chromatography (HPLC) consisting of a Chromaster instrument equipped with Aminex HPX-87H column (Bio-Rad) and a refractive index detector (Hitachi, Japan) was used to analyse the soluble products; 0.01 M H<sub>2</sub>SO<sub>4</sub> was used as the mobile phase at 0.5 ml min<sup>-1</sup> flow rate at 50 °C.<sup>10,26</sup> 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.<sup>13</sup>

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

152 Where  $\text{Conc}_p$  denotes the concentration of products (including disaccharide, glucose, fructose, LG,  
 153 HMF, LA, FA, and furfural);  $\text{MW}_p$  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<sub>2</sub>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),

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

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 <sup>13</sup>C nuclear magnetic resonance (NMR). Solid <sup>13</sup>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 <sup>13</sup>C NMR using D<sub>2</sub>O  
 168 solution. Chemical shifts ( $\delta$ ) 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)

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

## Results and discussion

### Catalytic conversion of bread waste under bio-derived and CO<sub>2</sub>-derived solvents

Facile conversion of bread waste was achieved under moderate reaction conditions, obtaining 45-72 mol% total product yield at  $130^{\circ}\text{C}$  under bio-derived and CO<sub>2</sub>-derived co-solvent systems (**Fig. 1a**). For H<sub>2</sub>O, PC/H<sub>2</sub>O, and GVL/H<sub>2</sub>O solvents, the maximum total sugars released from bread waste were 64-70 mol% in a short reaction duration of 1 min (**Fig. S1a**). In contrast, using IPA/H<sub>2</sub>O, the total sugar yield after 1 min of reaction was 43.5 mol%, increasing up to 48.8 mol% when the reaction was prolonged for 20 min. Given the total sugar yield generated at  $110^{\circ}\text{C}$  (**Fig. 1b**), hydrolysis of bread waste was faster in GVL/H<sub>2</sub>O (48.1 mol%) and PC/H<sub>2</sub>O (53.7 mol%) compared to H<sub>2</sub>O ( $\sim 30$  mol%) and IPA/H<sub>2</sub>O (9.4 mol%). With increasing reaction duration up to 20 min, sugar yield in H<sub>2</sub>O and IPA/H<sub>2</sub>O remained steady and generated an insignificant LA yield  $\sim 1.5$  mol% after 20 min of reaction. In contrast, sugars were consumed, and LA yield increased with increasing reaction duration gradually in GVL/H<sub>2</sub>O (up to 4.8 mol%) and sharply in PC/H<sub>2</sub>O (up to 19.6 mol%) (**Fig. 1a**). <sup>13</sup>C NMR spectra of reacted solutions (1 and 20 min reaction) (**Fig. 2a**) provided further evidence for the disparity in catalytic conversion under different solvent systems. <sup>13</sup>C NMR chemical shift ( $\delta$ ) at 95.8 ppm, attributed to glucose,<sup>28</sup> was observed for all reactions. The highest intensity of glucose peak was observed for 1 min reacted solution in PC/H<sub>2</sub>O, which agrees with the maximum sugar yield measured by HPLC. In contrast, the lowest intensity of glucose peak and emerged LA peak (at 27.7, 37.6, 177 pm) along with an FA peak (at 165.45 ppm)<sup>29</sup> for 20 min reaction in PC/H<sub>2</sub>O further prove the efficient tandem catalysis in PC/H<sub>2</sub>O. The characteristic peaks for LA and FA were not detectable in IPA/H<sub>2</sub>O and H<sub>2</sub>O, while

low-intensity peaks could be observed for GVL/H<sub>2</sub>O. Besides, representative solvent peaks<sup>29</sup> were detected in the reacted solutions indicated in **Fig. 2a**.

The higher soluble product yields in PC/H<sub>2</sub>O and GVL/H<sub>2</sub>O (**Fig. 1b**) could be related to the high reactivity of the Brønsted acid catalyst due to the availability of highly active proton in the presence of aprotic co-solvents in the reaction system.<sup>13,30</sup> The extent of proton stabilisation influences the acid dissociation constant, and in water lowers the proton reactivity, which subsequently elevates the required energy level for acid-catalysed biomass conversion reactions such as hydrolysis and dehydration.<sup>30</sup> Therefore, reaction kinetics could be slower in H<sub>2</sub>O (100%) compared to a solvent system consisting of a polar aprotic solvent such as GVL and PC, which might enhance the reaction rates owing to reactive proton and facile glycosidic bond cleavage.<sup>20,31</sup> For instance, a recent study reported a ten-fold increase in reaction rate for acid-catalysed conversion of HMF to LA using GVL with 10% H<sub>2</sub>O compared to 100% H<sub>2</sub>O as solvent.<sup>32</sup> Slower conversion of bread waste was observable in the case of IPA/H<sub>2</sub>O solvent (total sugar ~10 mol%, at 110°C, 1 min) (**Fig. 1b**), where both co-solvents are protic and probably hamper the proton reactivity during conversion.

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

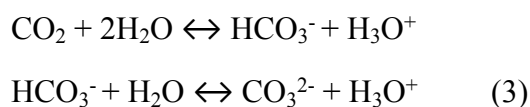
post-reaction solid residues shifted toward 98-103 ppm, presenting comparatively sharp peaks compared to the broad peak observed at 93-100 ppm for untreated bread waste. The broad shoulder observed around 95 ppm for untreated bread waste is characteristic of the amorphous domain of C1. In contrast, a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

## LA yield enhanced by in-vessel high pressure generated in PC/H<sub>2</sub>O

Comparing different co-solvent systems, PC/H<sub>2</sub>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.<sup>9,39</sup> Under GVL/H<sub>2</sub>O solvent, sugars depleted gradually during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H<sub>2</sub>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<sub>2</sub>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<sub>2</sub>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<sub>2</sub> as reported in the literature.<sup>13,40</sup> Noticeably, ~5-15% solvent loss was recorded for reactions in PC/H<sub>2</sub>O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the reaction. Besides, <sup>13</sup>C NMR spectra (**Fig. 2a**) for the reacted solutions under PC/H<sub>2</sub>O (1 and 20 min) showed peaks at 66.4 and 67.7 ppm representing PG.<sup>29</sup> 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<sub>2</sub> pressure recorded for more prolonged reactions in PC/H<sub>2</sub>O (**Fig. 3b**).

Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from CO<sub>2</sub> generation during catalytic conversion in PC/H<sub>2</sub>O might enhance the LA production rate. Another influential factor could be the increased acidity due to carbonic acid derived from partial

dissolution of CO<sub>2</sub> during the reaction, which might enhance sugar dehydration.<sup>41</sup> Solution acidity can arise through *in situ* formation and dissociation of carbonic acid, as given in Eq. (3).<sup>42</sup>



The acidity (pH) associated with CO<sub>2</sub> generated during 3-20 min reaction in PC/H<sub>2</sub>O was estimated, following the scheme reported in the literature.<sup>43-44</sup> The estimated CO<sub>2</sub>-derived pH value for specified reaction conditions was ~3.5, i.e., considerably higher than the H<sub>2</sub>SO<sub>4</sub> derived pH (~0.5) in this study. Therefore, CO<sub>2</sub>-derived pH on its own might not be sufficient to catalyse tandem reactions and significantly enhance LA yield. In other words, LA yield might be improved probably by PC/H<sub>2</sub>O generated CO<sub>2</sub> pressure more than CO<sub>2</sub>-derived acidity during the catalytic conversion of bread waste. To testify this postulation, an additional test using PC/H<sub>2</sub>O was conducted, in which autogenous pressure developed due to PC degradation (~22 bar) was released after 5 min reaction, and then the solution underwent reaction for another 15 min (**Fig. 3c**). Compared to continuous 20 min reaction in PC/H<sub>2</sub>O (LA yield 19.6 mol%), only about half of LA was produced (LA yield 11.2 mol%) when the pressure was released prematurely during the reaction. After the pressure release, the autogenous pressure was ~4.2 bar from the beginning till the end point of additional 15-min reaction. Moreover, supplementary tests using PG/H<sub>2</sub>O only generated ~3 mol% LA yield (130°C, 20 min) (**Fig. 3d**), which was insignificant compared to LA yield obtained in PC/H<sub>2</sub>O, therefore disproving any favourable influences by PG solvent (decomposed from PC) on the catalytic performance. These experimental evidences confirm the crucial enhancement of reaction pressure on the catalytic LA production.

## Intensification of LA yield through phase separation

Among co-solvent systems, PC/H<sub>2</sub>O 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<sub>2</sub>O and IPA/H<sub>2</sub>O (**Fig. 1a**), which could be further converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O, 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<sub>2</sub>O (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<sub>2</sub>O was only 6.6 mol% (150°C, 20 min) (**Fig. 4a**), notably lower than GVL/H<sub>2</sub>O system, corroborating the positive role of aprotic GVL solvent in enhancing proton reactivity for less energy-intensive tandem catalysis.<sup>10,30</sup>

The biphasic solvent systems (prepared using 30 wt% NaCl<sub>(aq)</sub>) 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<sub>2</sub>O and IPA/H<sub>2</sub>O 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<sub>2</sub>O and IPA/H<sub>2</sub>O. While biphasic GVL/H<sub>2</sub>O selectively generated LA as the main product 26.8 mol% yield and 4.4 mol% FA as co-product, IPA/H<sub>2</sub>O 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<sub>2</sub>O indicated that the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely



recommended solvent for HMF production, IPA can create a shielding effect around HMF that helps to prevent its rehydration and suppress further conversion to byproducts such as insoluble humins.<sup>45-46</sup> A recent study revealed that the rate constant for fructose to HMF was considerably higher than that of HMF to degradation products when IPA was present in the solvent system,<sup>46</sup> echoing the experimental observations in this study where low LA selectivity was obtained in IPA/H<sub>2</sub>O solvent system. In other words, IPA/H<sub>2</sub>O could be considered as a potential solvent for HMF production in future investigations. By contrast, in the presence of GVL solvent, H<sub>2</sub>SO<sub>4</sub> catalysed HMF production could be rapid and readily converted to LA at high acid strength.<sup>47</sup> Considerable LA yield achieved in biphasic GVL/H<sub>2</sub>O in this study (26.8 mol%, at 150°C, 20 min) proves the high efficiency of H<sub>2</sub>SO<sub>4</sub>/GVL/H<sub>2</sub>O system for LA production.

As GVL/H<sub>2</sub>O biphasic solvent was the most efficient for intensifying LA yield at moderate conditions, a comprehensive investigation was conducted for bread waste conversion in the co-solvent system following varied reaction conditions (150°C, 10-20 min). In biphasic GVL/H<sub>2</sub>O, LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H<sub>2</sub>O, 1:1) (**Fig. 5a**). However, a slight decrease in LA yield was observed after 20 min, suggesting that LA started to degrade with prolonged reaction. The major product in monophasic GVL/H<sub>2</sub>O (1:1, 15 min) was glucose (34.6 mol%), while the biphasic system selectively generated LA (~28 mol%) as the major product. The LA yield increased up to ~2.5 times in the biphasic system compared to the monophasic one (~11 mol%) (150°C, 15 min), implying that phase separation could be beneficial for intensive LA production and upscaling to industrial scale.

Essentially, to develop an efficient biphasic reaction medium, it is necessary to understand the contribution and influences of the reaction phase (H<sub>2</sub>O) and the extraction phase (GVL) to optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H<sub>2</sub>O

biphasic system, catalytic tests were conducted with various ratios of GVL and H<sub>2</sub>O (1:1, 1:3, and 3:1 of GVL/H<sub>2</sub>O). The partition coefficient for LA ( $R_{LA}$ ) in the GVL/H<sub>2</sub>O biphasic solvent was calculated to evaluate the effect of the extraction phase (GVL) in the system. The  $R_{LA}$  achieved for 10-15 min reaction was 4.2 when 1:1 GVL/H<sub>2</sub>O was applied for reaction (**Fig. 5b**), indicating a higher distribution of LA in the organic phase compared to the aqueous phase. Therefore, GVL solvent can be considered highly effective for reactive LA extraction. The partitioning of LA obtained in this study ( $R_{LA}$  4.2) is comparable to a previous study that reported  $R_{LA}$  ranging 3.7-4 using cellulose as feedstock.<sup>21</sup>

The total yield of LA increased (27.4-32 mol%) when a higher fraction of H<sub>2</sub>O (1:3, GVL/H<sub>2</sub>O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-17.1 mol%) when a lower fraction of H<sub>2</sub>O (3:1, GVL/H<sub>2</sub>O) was applied (**Fig. 5b**). Though the total LA yield increased with a higher fraction of H<sub>2</sub>O, the extraction of LA was found to be inefficient. The partition coefficient achieved was only 1.1 (1:3, GVL/H<sub>2</sub>O), indicating nearly even distribution of produced LA in the reaction and extraction phases due to the lower fraction of GVL applied. In comparison, ~97% of the total LA produced was extracted into the GVL phase when a higher fraction of GVL (3:1, GVL/H<sub>2</sub>O) was applied for reaction. However, a considerable decrease in total LA yield was observed, possibly due to the lack of sufficient aqueous phase available for reaction. These observations suggested the indispensable contribution of both reaction and extraction phases for an efficient biphasic system for LA production. Considering LA yield (27.4 mol%) and  $R_{LA}$  (4.2), the 1:1 GVL/H<sub>2</sub>O biphasic system (150°C, 15 min) provided the best performance for intensive LA production.

To reflect further on the mechanism and roles of catalytic species in NaCl modified GVL/H<sub>2</sub>O biphasic system, additional tests were performed under the selected reaction conditions.

In the case of reaction conducted with only NaCl (30 wt%) without acid catalyst, only marginal product yield was observed (**Fig. 6a**). When NaCl was applied together with H<sub>2</sub>SO<sub>4</sub> for bread waste conversion, an increase in LA yield was observed compared to the reaction in the presence of H<sub>2</sub>SO<sub>4</sub> without salt addition. These observations indicate that NaCl alone could not catalyse the desired reaction yet it may act synergistically with H<sub>2</sub>SO<sub>4</sub> enhancing the LA production in the aqueous phase during biphasic conversion of bread waste. Product distributions in the aqueous and GVL phases in the specified reaction conditions are provided in **Fig. S3**. The synergistic catalysis by NaCl and H<sub>2</sub>SO<sub>4</sub> together with simultaneous efficient extraction of LA into GVL could account for the high LA yield obtained in the GVL/H<sub>2</sub>O biphasic system.

Moreover, the recyclability of the aqueous phase containing H<sub>2</sub>SO<sub>4</sub> was investigated. After the catalytic run (reaction and cooling), the reacted organic phase was removed and fresh GVL and bread waste substrate were applied for another cycle of catalytic reaction (run-2) again while retaining the aqueous phase from the previous run without adding extra H<sub>2</sub>SO<sub>4</sub>. Similarly, the third cycle of catalytic reaction (run-3) was conducted. In the 2<sup>nd</sup> and 3<sup>rd</sup> run (**Fig. 6b**), 15 mol% and 13 mol% LA was obtained, respectively, compared to the LA yield (28 mol%) obtained in the initial run, which suggested that the acid catalyst could be retained in the aqueous phase and recycled for further conversion, though a certain degree of decrease in LA yield was observed. Future studies would be required for evaluating the biphasic system in a continuous reaction mode, which may be more efficient compared to the batch reaction mode.

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

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

### Perspectives on LA production and solvent recycling

To evaluate the efficiency of the catalytic system for LA production, LA yield relative to theoretical LA yield of bread waste substrate (considering total available carbohydrate and possible maximum theoretical yield (64.5%)) was calculated and compared with the reported achievements with commercially available starch substrates in the existing literature (**Table 1**). For PC/H<sub>2</sub>O (130°C, 20 min) and GVL/H<sub>2</sub>O biphasic solvents (150°C, 15 min), 45.7% and 66% LA yield was achieved relative to theoretical yield, respectively. This is considered promising in comparison to the reported LA yield (45.6-66.4%) from commercially available starch substrates in previous studies<sup>49-50</sup> where the conversion was conducted using comparatively harsh reaction conditions. For other recent studies where no direct comparison is possible due to the lack of data regarding relative LA yield,<sup>17,51</sup> it should be noted that much longer reaction duration was required to obtain the reported LA yield.

The recyclability of GVL/H<sub>2</sub>O biphasic solvent was investigated and discussed in the previous section. For PC/H<sub>2</sub>O solvent, despite partial decomposition of PC during acid catalysis, it offers various advantages as a solvent because a high product yield can be obtained with a moderate temperature and a short duration, which play a critical role in reducing the energy

consumption and reactor size. The production of PC from CO<sub>2</sub> is beneficial for process economy and environmental sustainability in terms of CO<sub>2</sub> utilisation. In the application of PC solvent, the derived CO<sub>2</sub> after reaction can be captured and recycled for PC production or other CO<sub>2</sub> based biorefineries, which are conducive to fostering the circular economy. The spent organic solvents can be recycled after separation and purification following commonly used techniques such as fractional distillation. For instance, a comprehensive life cycle assessment (LCA) on solvent waste recovery<sup>52</sup> demonstrated that implementing a solvent recovery system can reduce the environmental footprint of the total solvent manufacturing, usage, and disposal process. The energy requirements and emissions associated with the solvent recovery process have been recognised to be trivial in comparison to the emissions due to virgin solvent production and spent solvent disposal by incineration.

## Conclusions

This study provides comprehensive insights into the critical factors for intensive LA production, which can be conducive to the technology scale-up. The bio-derived and CO<sub>2</sub>-derived co-solvents in this study, i.e., PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, could facilitate H<sub>2</sub>SO<sub>4</sub> catalysed tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency. PC/H<sub>2</sub>O solvent was the most efficient for LA production using moderate reaction conditions, which could be attributed to the CO<sub>2</sub> pressure generated *in situ* through solvent (PC) degradation. Besides, catalytic performance could be significantly enhanced in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O using the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the final concentration of LA. GVL/H<sub>2</sub>O biphasic solvent seems promising considering LA yield (28 mol%) and LA partitioning ( $R_{LA}$  4.2) achieved in the study. The bio-derived and CO<sub>2</sub>-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

## 425 **Acknowledgements**

426 The authors appreciate the financial support from the Hong Kong International Airport  
427 Environmental Fund (Phase 2) and Hong Kong Research Grants Council (PolyU 15222020). The  
428 authors also acknowledge the support of the University Research Facility on Chemical and  
429 Environmental Analysis (UCEA) of PolyU.

## References

- (1) UNEP. Food Waste Index Report 2021 <http://www.unep.org/resources/report/unep-food-waste-index-report-2021> (accessed Apr 14, 2021).
- (2) Xiong, X.; Yu, I. K. M.; Tsang, D. C. W.; Bolan, N. S.; Ok, Y. S.; Igalavithana, A. D.; Kirkham, M. B.; Kim, K.-H.; Vikrant, K. Value-Added Chemicals from Food Supply Chain Wastes: State-of-the-Art Review and Future Prospects. *Chem. Eng. J.* **2019**, *375*, 121983. DOI:10.1016/j.cej.2019.121983
- (3) Mak, T. M. W.; Xiong, X.; Tsang, D. C. W.; Yu, I. K. M.; Poon, C. S. Sustainable Food Waste Management towards Circular Bioeconomy: Policy Review, Limitations and Opportunities. *Bioresour. Technol.* **2020**, *297*, 122497. DOI:10.1016/j.biortech.2019.122497.
- (4) Chen, S. S.; Maneerung, T.; Tsang, D. C. W.; Ok, Y. S.; Wang, C.-H. Valorization of Biomass to Hydroxymethylfurfural, Levulinic Acid, and Fatty Acid Methyl Ester by Heterogeneous Catalysts. *Chem. Eng. J.* **2017**, *328*, 246–273. DOI:10.1016/j.cej.2017.07.020.
- (5) Hayes, G. C.; Becer, C. R. Levulinic Acid: A Sustainable Platform Chemical for Novel Polymer Architectures. *Polym. Chem.* **2020**, *11*, 4068–4077. DOI:10.1039/D0PY00705F.
- (6) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Ng, Y. H.; Ok, Y. S.; Sherwood, J.; Clark, J. H. Green Synthesis of Gamma-Valerolactone (GVL) through Hydrogenation of Biomass-Derived Levulinic Acid Using Non-Noble Metal Catalysts: A Critical Review. *Chem. Eng. J.* **2019**, *372*, 992–1006. DOI:10.1016/j.cej.2019.04.199.
- (7) Antonetti, C.; Licursi, D.; Fulignati, S.; Valentini, G.; Raspolli Galletti, A. New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock. *Catalysts* **2016**, *6*, 196. DOI:10.3390/catal6120196.
- (8) Pileidis, F. D.; Titirici, M.-M. Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. *ChemSusChem* **2016**, *9*, 562–582. DOI:10.1002/cssc.201501405.
- (9) Chen, S. S.; Yu, I. K. M.; Tsang, D. C. W.; Yip, A. C. K.; Khan, E.; Wang, L.; Ok, Y. S.; Poon, C. S. Valorization of Cellulosic Food Waste into Levulinic Acid synthesized by Heterogeneous Brønsted Acids: Temperature and Solvent Effects. *Chem. Eng. J.* **2017**, *327*, 328–335. DOI:10.1016/j.cej.2017.06.108
- (10) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Su, Z.; Hu, C.; Wu, K. C. W.; Yip, A. C. K.; Ok, Y. S.; Poon, C. S. Influence of Green Solvent on Levulinic Acid Production from Lignocellulosic Paper Waste. *Bioresour. Technol.* **2020**, *298*, 122544. DOI:10.1016/j.biortech.2019.122544.
- (11) Yu, I. K. M.; Fan, J.; Budarin, V. L.; Bouxin, F. P.; Clark, J. H.; Tsang, D. C. W. NaCl-Promoted Phase Transition and Glycosidic Bond Cleavage under Microwave Heating for Energy-Efficient Biorefinery of Rice Starch. *Green Chem.* **2020**, *22*, 7355–7365. DOI:10.1039/D0GC01761B.
- (12) Yu, I. K. M.; Tsang, D. C. W.; Chen, S. S.; Wang, L.; Hunt, A. J.; Sherwood, J.; De Oliveira Vigier, K.; Jérôme, F.; Ok, Y. S.; Poon, C. S. Polar Aprotic Solvent-Water Mixture as the Medium for Catalytic Production of Hydroxymethylfurfural (HMF) from Bread Waste. *Bioresour. Technol.* **2017**, *245*, 456–462. DOI:10.1016/j.biortech.2017.08.170.
- (13) Yu, I. K. M.; Tsang, D. C. W.; Yip, A. C. K.; Hunt, A. J.; Sherwood, J.; Shang, J.; Song, H.; Ok, Y. S.; Poon, C. S. Propylene Carbonate and  $\gamma$ -Valerolactone as Green Solvents

- Enhance Sn(IV)-Catalysed Hydroxymethylfurfural (HMF) Production from Bread Waste. *Green Chem.* **2018**, *20*, 2064–2074. DOI:10.1039/C8GC00358K.
- (14) Antonetti, C.; Licursi, D.; Raspolli Galletti, A. M. New Intensification Strategies for the Direct Conversion of Real Biomass into Platform and Fine Chemicals: What Are the Main Improvable Key Aspects? *Catalysts* **2020**, *10*, 961. DOI:10.3390/catal10090961.
- (15) Chen, S. S.; Wang, L.; Yu, I. K. M.; Tsang, D. C. W.; Hunt, A. J.; Jérôme, F.; Zhang, S.; Ok, Y. S.; Poon, C. S. Valorization of Lignocellulosic Fibres of Paper Waste into Levulinic Acid Using Solid and Aqueous Brønsted Acid. *Bioresour. Technol.* **2018**, *247*, 387–394. DOI:10.1016/j.biortech.2017.09.110.
- (16) Dyson, P. J.; Jessop, P. G. Solvent Effects in Catalysis: Rational Improvements of Catalysts via Manipulation of Solvent Interactions. *Catal. Sci. Technol.* **2016**, *6*, 3302–3316. DOI:10.1039/C5CY02197A.
- (17) Lui, M. Y.; Wong, C. Y. Y.; Choi, A. W.-T.; Mui, Y. F.; Qi, L.; Horváth, I. T. Valorization of Carbohydrates of Agricultural Residues and Food Wastes: A Key Strategy for Carbon Conservation. *ACS Sustain. Chem. Eng.* **2019**, *7*, 17799–17807. DOI:10.1021/acssuschemeng.9b04242.
- (18) Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C. R.; Abou-Shehadeh, S.; Dunn, P. J. CHEM21 Selection Guide of Classical- and Less Classical-Solvents. *Green Chem.* **2016**, *18*, 288–296. DOI:10.1039/C5GC01008J.
- (19) Gao, F.; Bai, R.; Ferlin, F.; Vaccaro, L.; Li, M.; Gu, Y. Replacement Strategies for Non-Green Dipolar Aprotic Solvents. *Green Chem.* **2020**, *22*, 6240–6257. DOI:10.1039/D0GC02149K.
- (20) Dutta, S.; Yu, I. K. M.; Tsang, D. C. W.; Fan, J.; Clark, J. H.; Jiang, Z.; Su, Z.; Hu, C.; Poon, C. S. Efficient Depolymerization of Cellulosic Paper Towel Waste Using Organic Carbonate Solvents. *ACS Sustain. Chem. Eng.* **2020**, *8*, 13100–13110. DOI:10.1021/acssuschemeng.0c04102.
- (21) Wettstein, S. G.; Alonso, D. M.; Chong, Y.; Dumesic, J. A. Production of Levulinic Acid and Gamma-Valerolactone (GVL) from Cellulose Using GVL as a Solvent in Biphasic Systems. *Energy Environ. Sci.* **2012**, *5*, 8199. DOI:10.1039/c2ee22111j.
- (22) Wang, J.; Cui, H.; Wang, Y.; Zhao, R.; Xie, Y.; Wang, M.; Yi, W. Efficient Catalytic Conversion of Cellulose to Levulinic Acid in the Biphasic System of Molten Salt Hydrate and Methyl Isobutyl Ketone. *Green Chem.* **2020**, *22*, 4240–4251. DOI:10.1039/D0GC00897D.
- (23) Rihko-Struckmann, L. K.; Oluyinka, O.; Sahni, A.; McBride, K.; Fachet, M.; Ludwig, K.; Sundmacher, K. Transformation of Remnant Algal Biomass to 5-HMF and Levulinic Acid: Influence of a Biphasic Solvent System. *RSC Adv.* **2020**, *10*, 24753–24763. DOI:10.1039/D0RA02784G.
- (24) Kumar, S.; Ahluwalia, V.; Kundu, P.; Sangwan, R. S.; Kansal, S. K.; Runge, T. M.; Elumalai, S. Improved Levulinic Acid Production from Agri-Residue Biomass in Biphasic Solvent System through Synergistic Catalytic Effect of Acid and Products. *Bioresour. Technol.* **2018**, *251*, 143–150. DOI:10.1016/j.biortech.2017.12.033.
- (25) Jiang, Z.; Remón, J.; Li, T.; Budarin, V. L.; Fan, J.; Hu, C.; Clark, J. H. A One-Pot Microwave-Assisted NaCl–H<sub>2</sub>O/GVL Solvent System for Cellulose Conversion to 5-Hydroxymethylfurfural and Saccharides with in Situ Separation of the Products. *Cellulose* **2019**, *26*, 8383–8400. DOI:10.1007/s10570-019-02362-8.

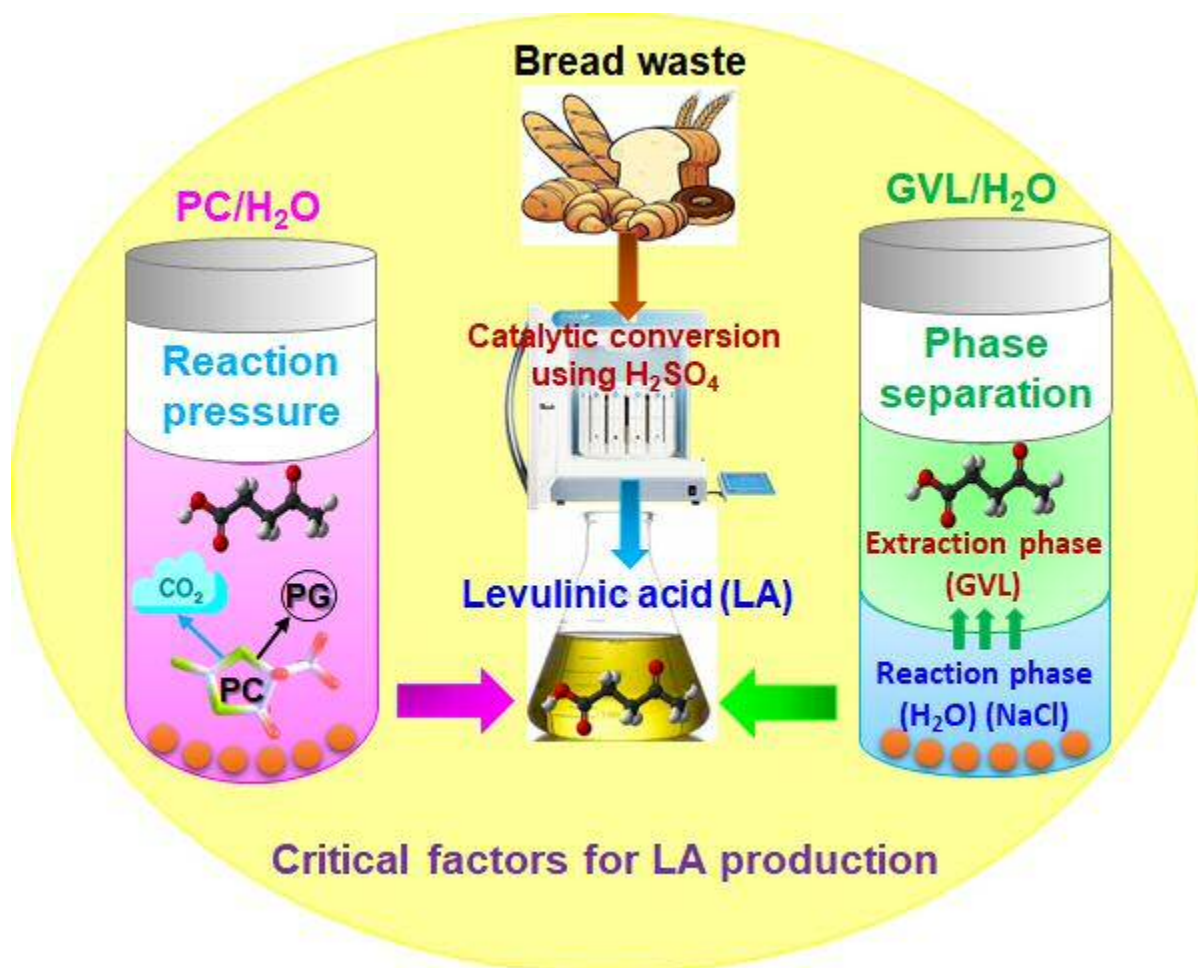


- (26) Yu, I. K. M.; Xiong, X.; Tsang, D. C. W.; Ng, Y. H.; Clark, J. H.; Fan, J.; Zhang, S.; Hu, C.; Ok, Y. S. Graphite Oxide- and Graphene Oxide-Supported Catalysts for Microwave-Assisted Glucose Isomerisation in Water. *Green Chem.* **2019**, *21*, 4341–4353. DOI:10.1039/C9GC00734B.
- (27) Foresti, M. L.; Williams, M. del P.; Martínez-García, R.; Vázquez, A. Analysis of a Preferential Action of  $\alpha$ -Amylase from *B. Licheniformis* towards Amorphous Regions of Waxy Maize Starch. *Carbohydr. Polym.* **2014**, *102*, 80–87. DOI:10.1016/j.carbpol.2013.11.013.
- (28) Qi, L.; Alamillo, R.; Elliott, W. A.; Andersen, A.; Hoyt, D. W.; Walter, E. D.; Han, K. S.; Washton, N. M.; Rioux, R. M.; Dumesic, J. A.; Scott, S. L. Operando Solid-State NMR Observation of Solvent-Mediated Adsorption-Reaction of Carbohydrates in Zeolites. *ACS Catal.* **2017**, *7*, 3489–3500. DOI:10.1021/acscatal.7b01045.
- (29) AIST. Spectral Database for Organic Compounds (SDBS). **2018**, [https://sdb.sdb.aist.go.jp/sdb/cgi-bin/cre\\_index.cgi](https://sdb.sdb.aist.go.jp/sdb/cgi-bin/cre_index.cgi) (accessed May 10, 2021).
- (30) Mellmer, M. A.; Sener, C.; Gallo, J. M. R.; Luterbacher, J. S.; Alonso, D. M.; Dumesic, J. A. Solvent Effects in Acid-Catalyzed Biomass Conversion Reactions. *Angew. Chem. Int. Ed.* **2014**, *53*, 11872–11875. DOI:10.1002/anie.201408359.
- (31) Mellmer, M. A.; Alonso, D. M.; Luterbacher, J. S.; Gallo, J. M. R.; Dumesic, J. A. Effects of  $\gamma$ -Valerolactone in Hydrolysis of Lignocellulosic Biomass to Monosaccharides. *Green Chem.* **2014**, *16*, 4659–4662. DOI:10.1039/C4GC01768D.
- (32) Mellmer, M. A.; Sanpitakserree, C.; Demir, B.; Bai, P.; Ma, K.; Neurock, M.; Dumesic, J. A. Solvent-Enabled Control of Reactivity for Liquid-Phase Reactions of Biomass-Derived Compounds. *Nat. Catal.* **2018**, *1* (3), 199–207. DOI:10.1038/s41929-018-0027-3.
- (33) Flanagan, B. M.; Gidley, M. J.; Warren, F. J. Rapid Quantification of Starch Molecular Order through Multivariate Modelling of  $^{13}\text{C}$  CP/MAS NMR Spectra. *Chem. Commun.* **2015**, *51*, 14856–14858. DOI:10.1039/C5CC06144J.
- (34) Cai, J.; Cai, C.; Man, J.; Yang, Y.; Zhang, F.; Wei, C. Crystalline and Structural Properties of Acid-Modified Lotus Rhizome C-Type Starch. *Carbohydr. Polym.* **2014**, *102*, 799–807. DOI:10.1016/j.carbpol.2013.10.088.
- (35) Atichokudomchai, N.; Varavinit, S.; Chinachoti, P. A Study of Ordered Structure in Acid-Modified Tapioca Starch by C CP/MAS Solid-State NMR. *Carbohydr. Polym.* **2004**, *58*, 383–389. DOI:10.1016/j.carbpol.2004.07.017.
- (36) Mutungi, C.; Passauer, L.; Onyango, C.; Jaros, D.; Rohm, H. Debranched Cassava Starch Crystallinity Determination by Raman Spectroscopy: Correlation of Features in Raman Spectra with X-Ray Diffraction and  $^{13}\text{C}$  CP/MAS NMR Spectroscopy. *Carbohydr. Polym.* **2012**, *87*, 598–606. DOI:10.1016/j.carbpol.2011.08.032.
- (37) Morrison, W. R.; Tester, R. F.; Gidley, M. J.; Karkalas, J. Resistance to Acid Hydrolysis of Lipid-Complexed Amylose and Lipid-Free Amylose in Lintnerised Waxy and Non-Waxy Barley Starches. *Carbohydr. Res.* **1993**, *245*, 289–302. DOI:10.1016/0008-6215(93)80078-S.
- (38) Hoover, R. Acid-treated Starches. *Food Rev. Int.* **2000**, *16*, 369–392. DOI: 10.1081/FRI-100100292.
- (39) Lappalainen, K.; Vogeler, N.; Kärkkäinen, J.; Dong, Y.; Niemelä, M.; Rusanen, A.; Ruotsalainen, A. L.; Wäli, P.; Markkola, A.; Lassi, U. Microwave-Assisted Conversion of Novel Biomass Materials into Levulinic Acid. *Biomass Convers. Biorefinery* **2018**, *8*, 965–970. DOI:10.1007/s13399-018-0334-6.

- (40) Zhang, Z.; O'Hara, I. M.; Rackemann, D. W.; Doherty, W. O. S. Low Temperature Pretreatment of Sugarcane Bagasse at Atmospheric Pressure Using Mixtures of Ethylene Carbonate and Ethylene Glycol. *Green Chem* **2013**, *15*, 255–264. DOI:10.1039/C2GC36323B.
- (41) Morais, A. R. C.; Matuchaki, M. D. D. J.; Andreus, J.; Bogel-Lukasik, R. A Green and Efficient Approach to Selective Conversion of Xylose and Biomass Hemicellulose into Furfural in Aqueous Media Using High-Pressure CO<sub>2</sub> as a Sustainable Catalyst. *Green Chem.* **2016**, *18*, 2985–2994. DOI:10.1039/C6GC00043F.
- (42) Jing, S.; Cao, X.; Zhong, L.; Peng, X.; Zhang, X.; Wang, S.; Sun, R. In Situ Carbonic Acid from CO<sub>2</sub>: A Green Acid for Highly Effective Conversion of Cellulose in the Presence of Lewis Acid. *ACS Sustain. Chem. Eng.* **2016**, *4*, 4146–4155. DOI:10.1021/acssuschemeng.6b00623.
- (43) Van Walsum, G. P. Severity Function Describing the Hydrolysis of Xylan Using Carbonic Acid. In *Twenty-Second Symposium on Biotechnology for Fuels and Chemicals*; Davison, B. H., McMillan, J., Finkelstein, M., Eds.; ABAB Symposium; Humana Press: Totowa, NJ, **2001**, DOI:10.1007/978-1-4612-0217-2\_27.
- (44) Toscan, A.; Morais, A. R. C.; Paixão, S. M.; Alves, L.; Andreus, J.; Camassola, M.; Dillon, A. J. P.; Lukasik, R. M. High-Pressure Carbon Dioxide/Water Pre-Treatment of Sugarcane Bagasse and Elephant Grass: Assessment of the Effect of Biomass Composition on Process Efficiency. *Bioresour. Technol.* **2017**, *224*, 639–647. DOI:10.1016/j.biortech.2016.11.101.
- (45) Mushrif, S. H.; Caratzoulas, S.; Vlachos, D. G. Understanding Solvent Effects in the Selective Conversion of Fructose to 5-Hydroxymethyl-Furfural: A Molecular Dynamics Investigation. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2637. DOI:10.1039/c2cp22694d.
- (46) Agutaya, J. K. C. N.; Inoue, R.; Vin Tsie, S. S.; Quitain, A. T.; de la Peña-García, J.; Pérez-Sánchez, H.; Sasaki, M.; Kida, T. Metal-Free Synthesis of HMF from Glucose Using the Supercritical CO<sub>2</sub>–Subcritical H<sub>2</sub>O–Isopropanol System. *Ind. Eng. Chem. Res.* **2020**, *59*, 16527–16538. DOI:10.1021/acs.iecr.0c03551.
- (47) Qi, L.; Mui, Y. F.; Lo, S. W.; Lui, M. Y.; Akien, G. R.; Horváth, I. T. Catalytic Conversion of Fructose, Glucose, and Sucrose to 5-(Hydroxymethyl)Furfural and Levulinic and Formic Acids in  $\gamma$ -Valerolactone As a Green Solvent. *ACS Catal.* **2014**, *4*, 1470–1477. DOI:10.1021/cs401160y.
- (48) Flannelly, T.; Lopes, M.; Kupiainen, L.; Dooley, S.; Leahy, J. J. Non-Stoichiometric Formation of Formic and Levulinic Acids from the Hydrolysis of Biomass Derived Hexose Carbohydrates. *RSC Adv.* **2016**, *6*, 5797–5804. DOI:10.1039/C5RA25172A.
- (49) Fang, Q.; Hanna, M. A. Experimental Studies for Levulinic Acid Production from Whole Kernel Grain Sorghum. *Bioresour. Technol.* **2002**, *81*, 187–192. DOI:10.1016/S0960-8524(01)00144-4.
- (50) Cha, J. Y.; Hanna, M. A. Levulinic Acid Production Based on Extrusion and Pressurized Batch Reaction. *Ind. Crops Prod.* **2002**, *16*, 109–118. DOI:10.1016/S0926-6690(02)00033-X.
- (51) Vyver, S. V. de; Thomas, J.; Geboers, J.; Keyzer, S.; Smet, M.; Dehaen, W.; A. Jacobs, P.; F. Sels, B. Catalytic Production of Levulinic Acid from Cellulose and Other Biomass-Derived Carbohydrates with Sulfonated Hyperbranched Poly(Arylene Oxindole)s. *Energy Environ. Sci.* **2011**, *4*, 3601–3610. DOI:10.1039/C1EE01418H.

- 611 (52) Raymond, M. J.; Slater, C. S.; Savelski, M. J. LCA Approach to the Analysis of Solvent  
612 Waste Issues in the Pharmaceutical Industry. *Green Chem.* **2010**, *12*, 1826–1834.  
613 DOI:10.1039/C003666H.  
614

## Table of Content



## Synopsis:

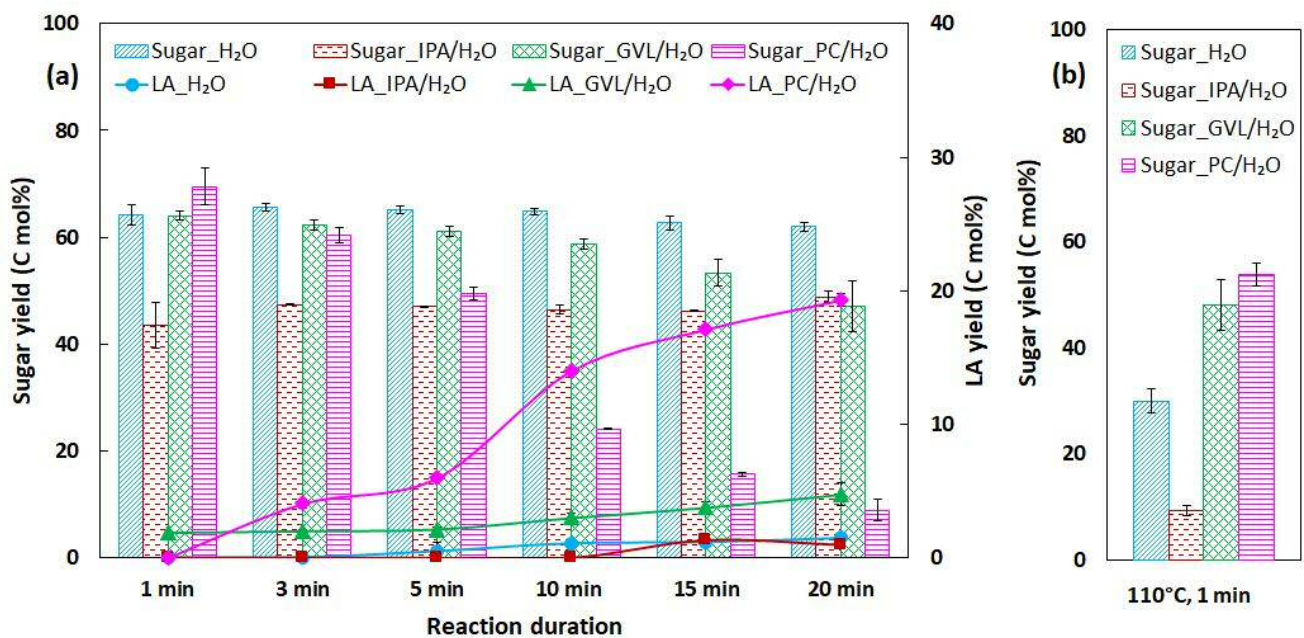
This study provides new and critical insights into sustainable catalytic conversion of food (bread) waste to platform chemicals for achieving sustainable development goals and fostering a circular economy.

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

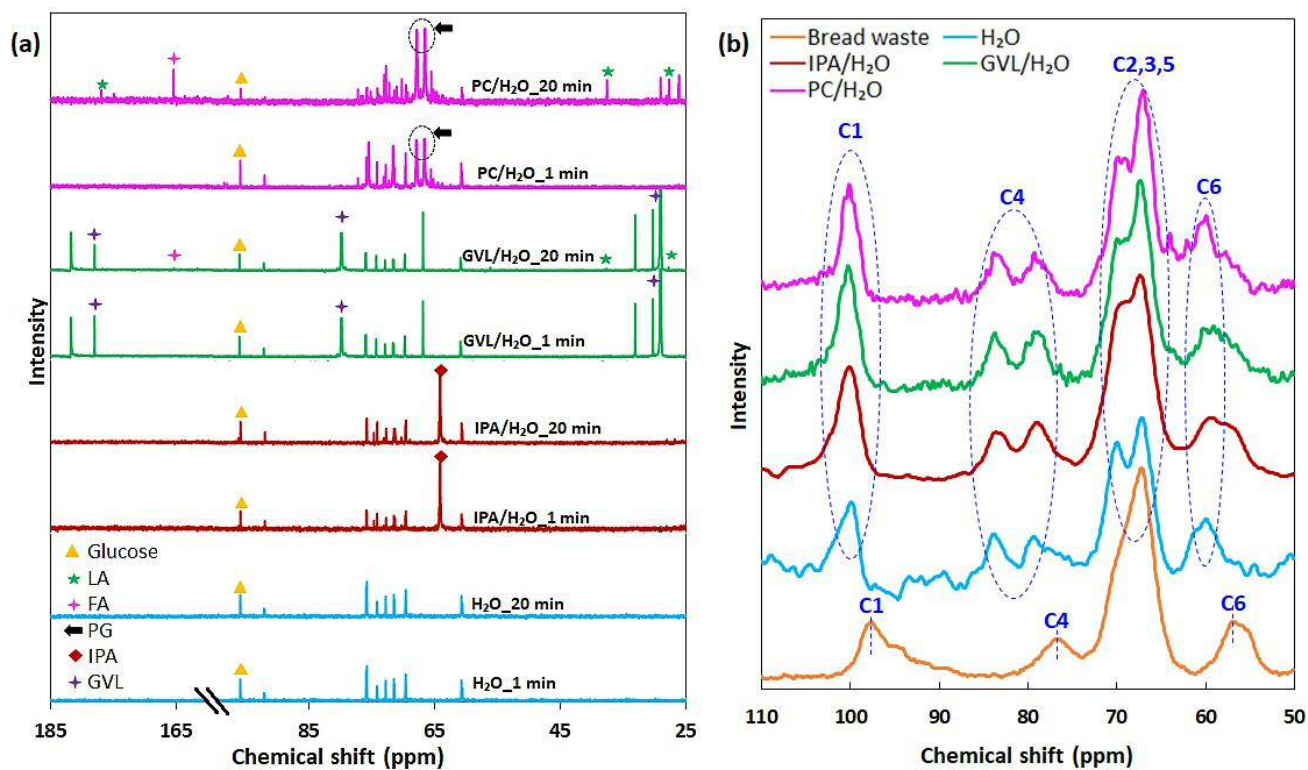
### Solvent effects, reaction pressure and phase separation

#### 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<sub>2</sub>SO<sub>4</sub>, 130°C, 1:1 solvent ratio).
- Fig. 2.** (a) <sup>13</sup>C NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 1 min & 20 min, 1:1 solvent ratio), (b) <sup>13</sup>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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H<sub>2</sub>O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H<sub>2</sub>O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>O (monophasic) and (b) GVL/H<sub>2</sub>O (monophasic); (c) comparative product yields in IPA/H<sub>2</sub>O and GVL/H<sub>2</sub>O monophasic and biphasic medium (30 wt% NaCl<sub>(aq)</sub>) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1:1 solvent ratio).
- Fig. 5.** (a) Product yields during the catalytic conversion of bread waste in GVL/H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 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<sub>2</sub>O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 15 min, solvent ratio 1:1).

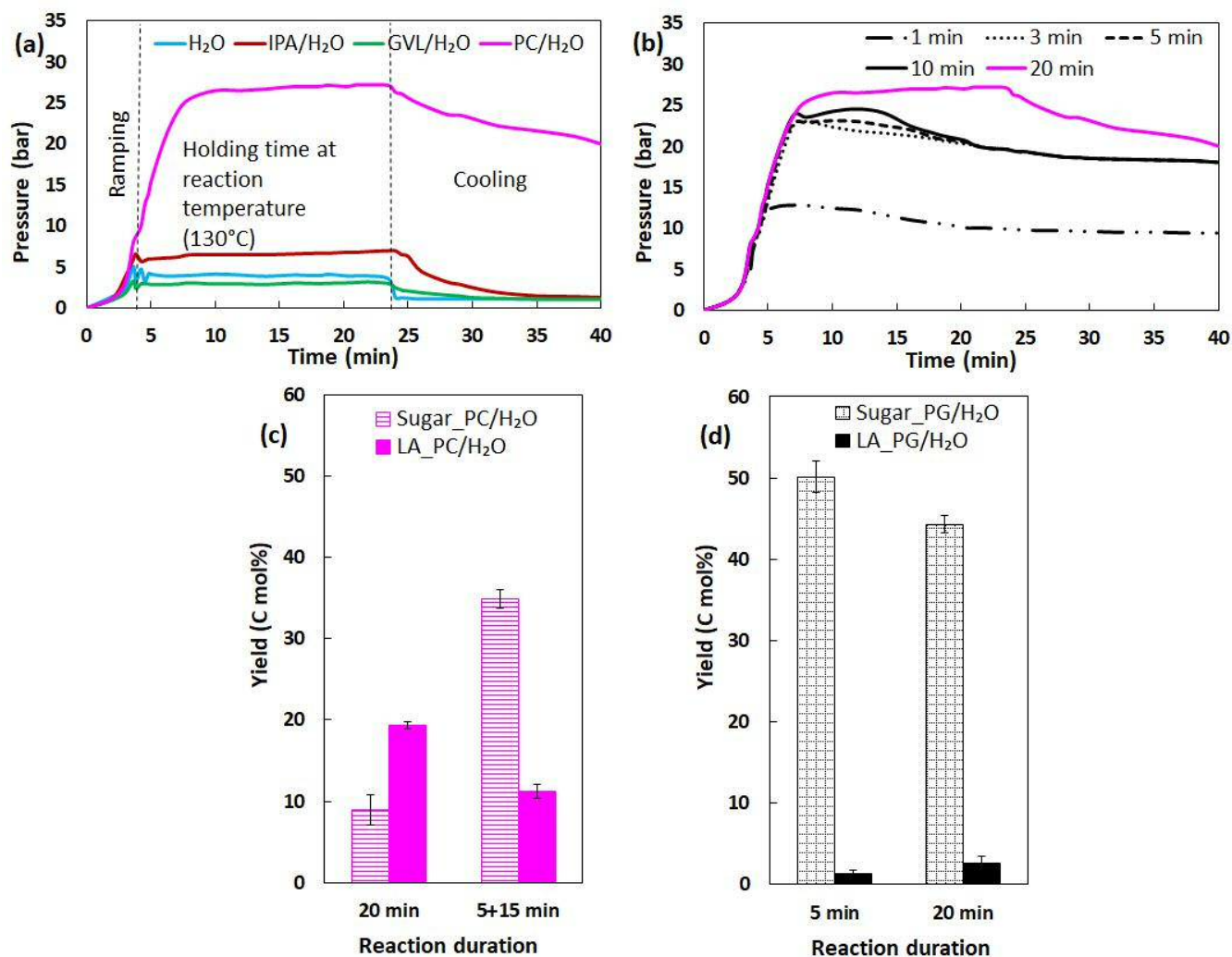


**Fig. 1.** Total sugar yield and LA yield during the catalytic conversion of bread waste in different solvents (a) at 130°C, 1-20 min, (b) at 110°C, 1 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 1:1 solvent ratio).



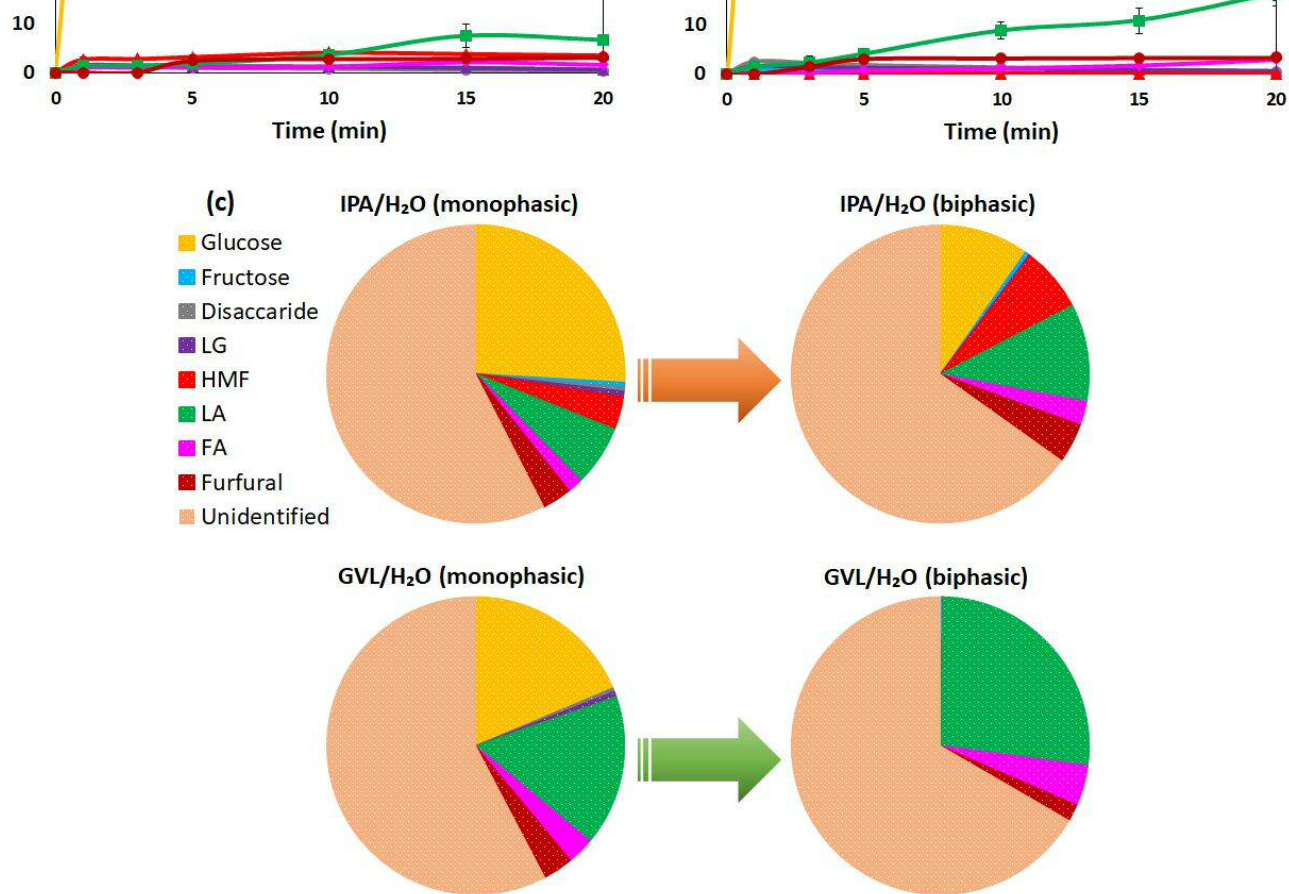
**Fig. 2.** (a)  $^{13}\text{C}$  NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M  $\text{H}_2\text{SO}_4$ , 130°C, 1 min & 20 min, 1:1 solvent ratio), (b)  $^{13}\text{C}$  solid-state NMR spectra of untreated bread waste and solid residues collected after reaction under different solvent systems (Reaction conditions: 5 wt% substrate loading, 0.5 M  $\text{H}_2\text{SO}_4$ , 130°C, 20 min, 1:1 solvent ratio).



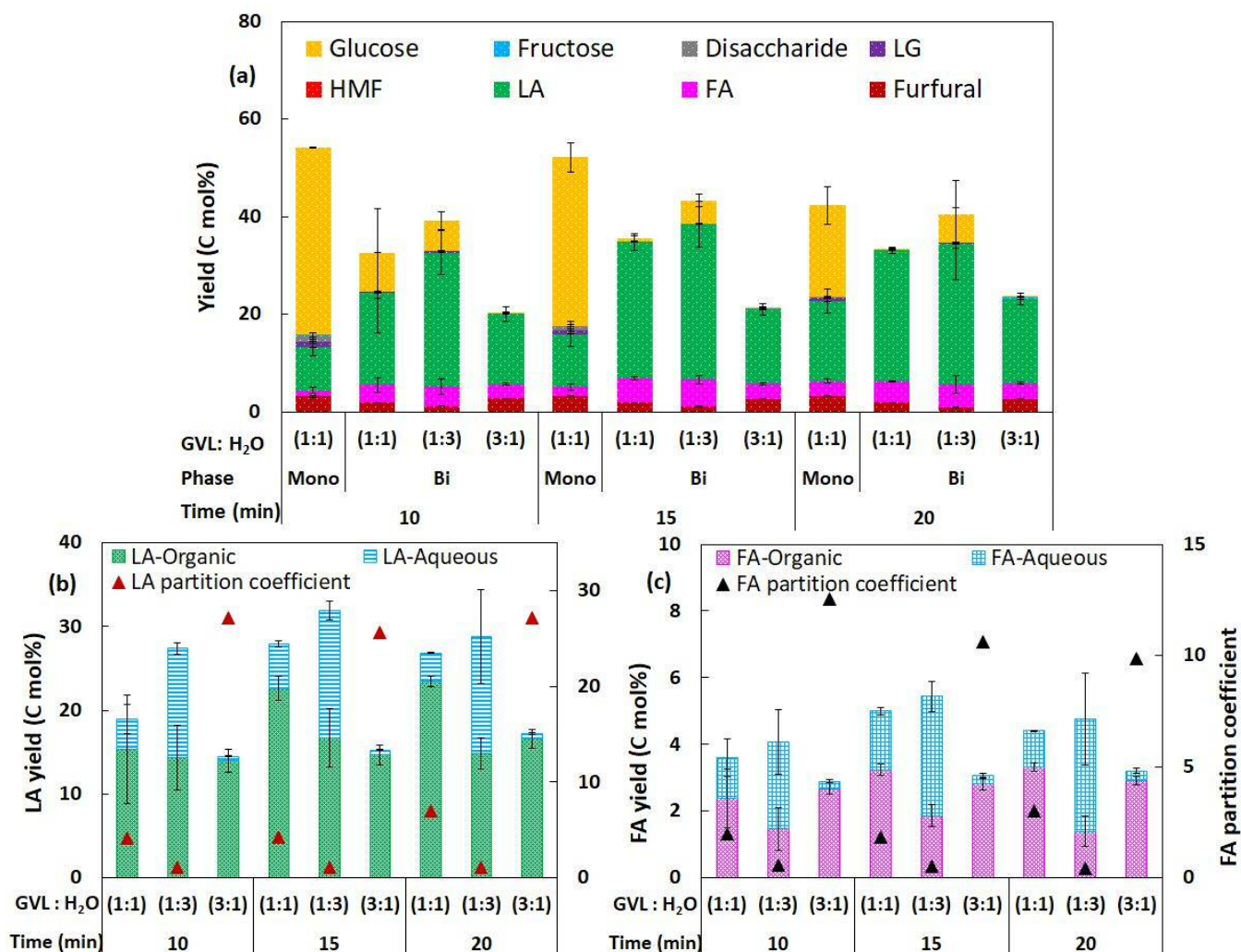


**Fig. 3.** (a) Pressure profile during the catalytic conversion of bread waste in different solvents for 20 min reaction, (b) pressure profile in PC/H<sub>2</sub>O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H<sub>2</sub>O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H<sub>2</sub>O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 1:1 solvent ratio).

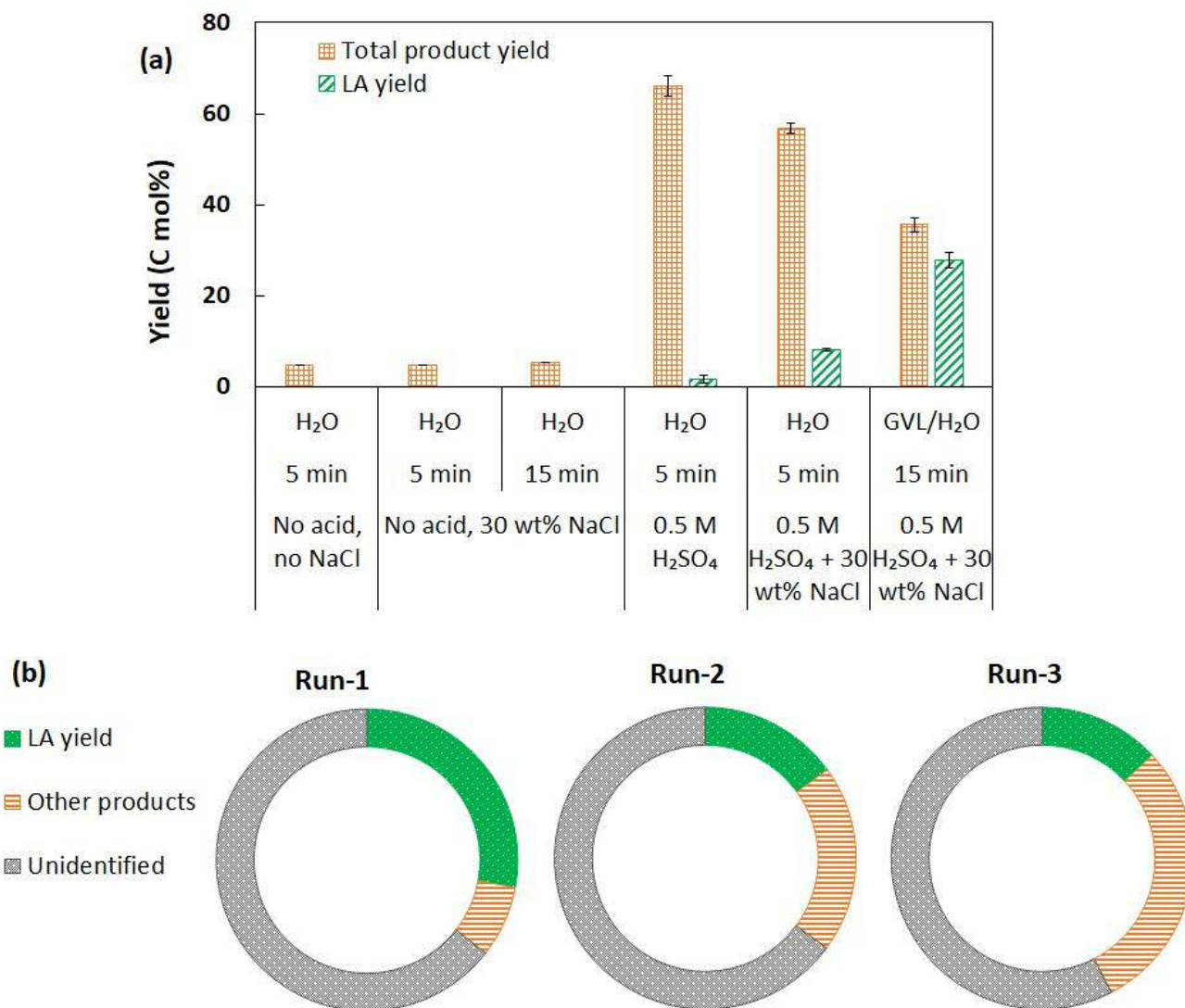




**Fig. 4.** Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H<sub>2</sub>O (monophasic) and (b) GVL/H<sub>2</sub>O (monophasic); (c) comparative product yields in IPA/H<sub>2</sub>O and GVL/H<sub>2</sub>O monophasic and biphasic medium (30 wt% NaCl<sub>(aq)</sub>) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1:1 solvent ratio).



**Fig. 5.** (a) Product yields during the catalytic conversion of bread waste in GVL/H<sub>2</sub>O 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<sub>2</sub>O biphasic medium comprising different solvent ratio (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 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/H<sub>2</sub>O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 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 literature (mol%)
Bread waste	130°C, 20 min, H <sub>2</sub> O	0.5 M H <sub>2</sub> SO <sub>4</sub>	1.5	1.2	2
	130°C, 20 min, IPA/H <sub>2</sub> O		1.0	0.8	2
	130°C, 20 min, GVL/H <sub>2</sub> O		4.8	3.8	1
	130°C, 20 min, PC/H <sub>2</sub> O		19.6	15.5	4
	150°C, 20 min, IPA/H <sub>2</sub> O (mono)		6.6	5.3	1
	150°C, 20 min, IPA/H <sub>2</sub> O (bi)		10.6	8.5	2
	150°C, 15 min, GVL/H <sub>2</sub> O (mono)		10.9	8.8	2
	150°C, 15 min, GVL/H <sub>2</sub> O (bi)		27.9	22.4	6
	150°C, 20 min, GVL/H <sub>2</sub> O (mono)		16.4	13.2	3
	150°C, 20 min, GVL/H <sub>2</sub> O (bi)		26.8	21.6	6
Bread	130°C, 8 h	1.5 ml 5 M H <sub>2</sub> SO <sub>4</sub> 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 <sub>2</sub> SO <sub>4</sub>	-	47.5	6
Sorghum grain	200°C, 40 min	8% H <sub>2</sub> SO <sub>4</sub>		32.6	4

## Supplementary Information

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

Shanta Dutta <sup>a</sup>, Iris K.M. Yu <sup>a,b</sup>, Jiajun Fan <sup>c</sup>, James H. Clark <sup>c</sup>, and Daniel C.W. Tsang <sup>a,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 181 Chatham Road South, Hung Hom, Kowloon, Hong Kong, China.

<sup>b</sup> Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany.

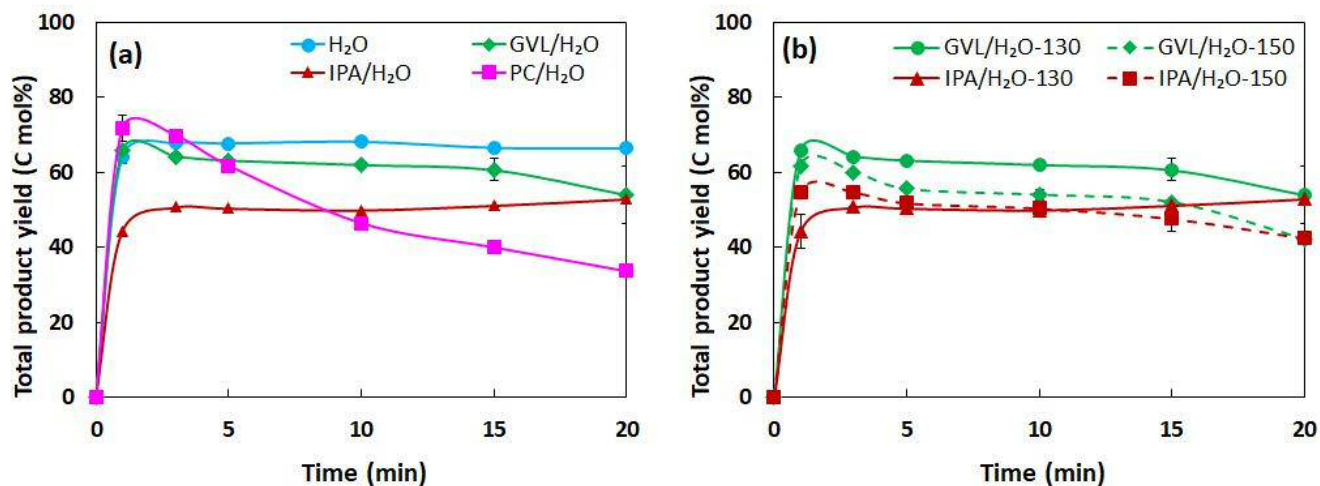
<sup>c</sup> Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK.

\*Corresponding author, [dan.tsang@polyu.edu.hk](mailto:dan.tsang@polyu.edu.hk)

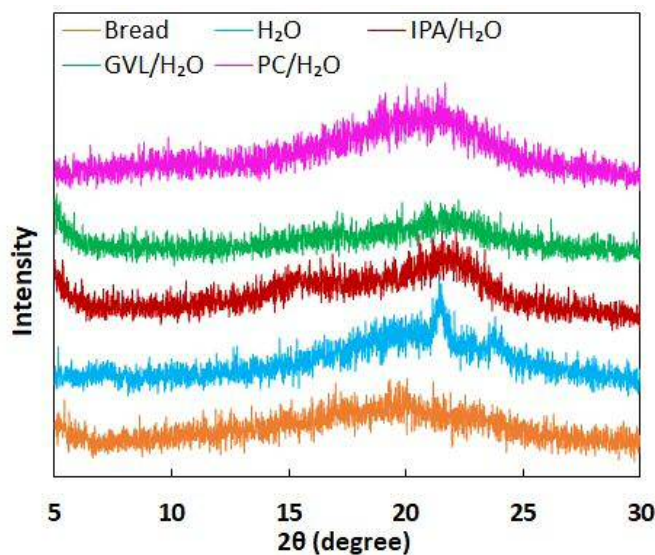
**List of Figures:**

- 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<sub>2</sub>O and IPA/H<sub>2</sub>O (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 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/H<sub>2</sub>O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 20 min).

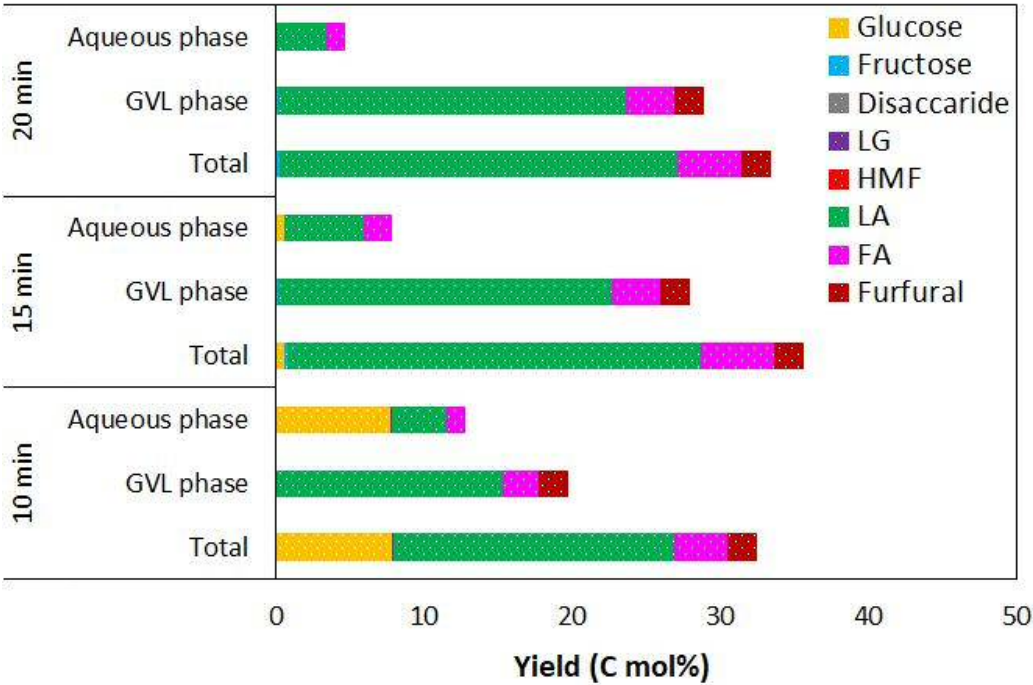




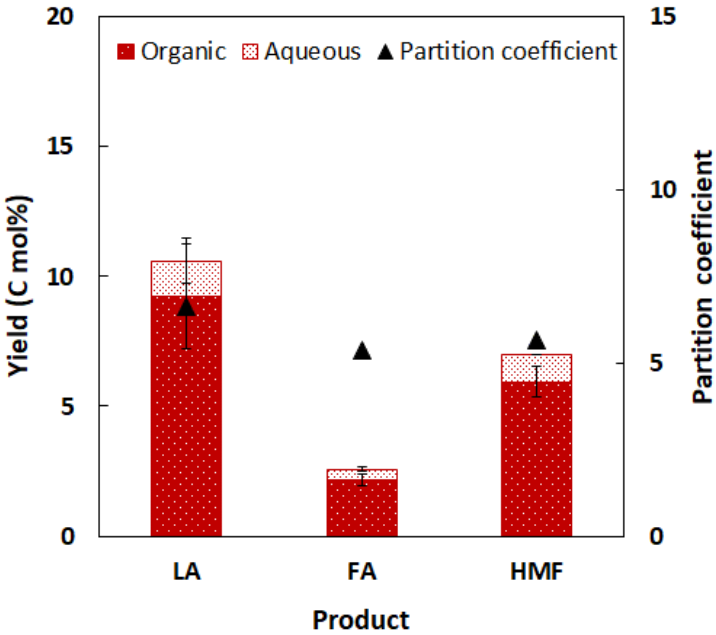
**Fig. S1.** Total product yields during the catalytic conversion of bread waste under different solvents at (a) at 130°C and (b) at 130°C and 150°C under GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1-20 min, 1:1 solvent 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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 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/H<sub>2</sub>O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 20 min).