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## Efficient Depolymerization of Cellulosic Paper Towel Waste Using Organic Carbonate Solvents

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# Efficient Depolymerization of Cellulosic Paper Towel Waste Using Organic Carbonate Solvents

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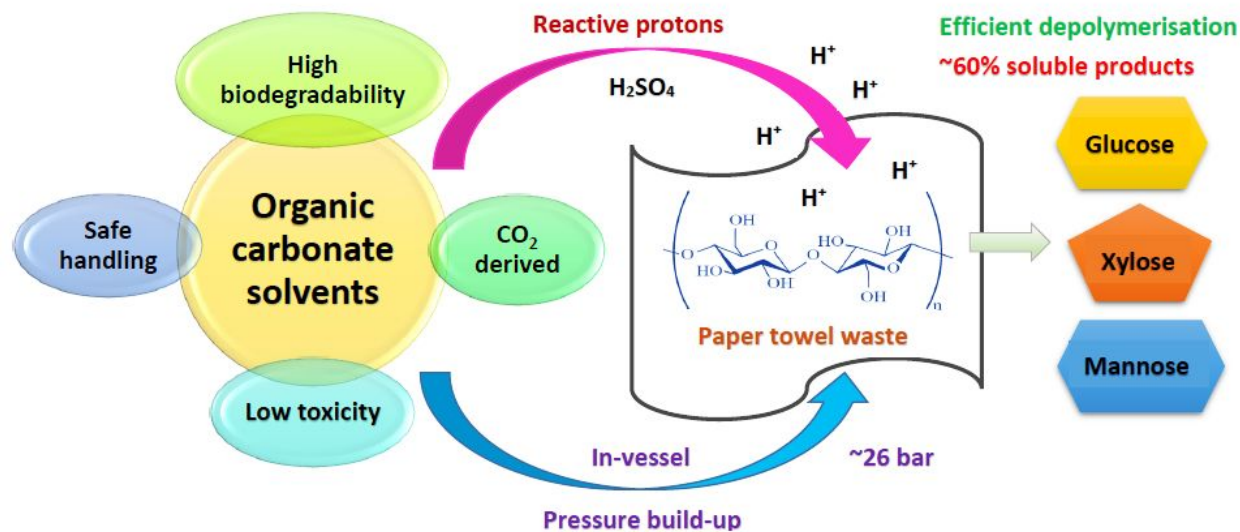
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## 1 **Abstract**

2 Efficient depolymerization of lignocellulosic biomass is a prerequisite for sugar production and its  
3 subsequent up-gradation to fuels and chemicals. Organic carbonate solvents, i.e., propylene  
4 carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC), which are low in  
5 toxicity and biodegradable, were investigated as ‘green’ co-solvents (PC/H<sub>2</sub>O, EC/H<sub>2</sub>O,  
6 DMC/H<sub>2</sub>O, solvent ratio 1:1) for depolymerization of cellulosic paper towel waste. PC/H<sub>2</sub>O and  
7 EC/H<sub>2</sub>O enhanced the depolymerization of paper towel waste and improved the total sugar yield  
8 (up to ~25 Cmol%) compared to H<sub>2</sub>O only (up to ~11 Cmol%) at mild reaction conditions (130°C,  
9 20 min). The higher performance of PC/H<sub>2</sub>O and EC/H<sub>2</sub>O can be attributed to higher availability  
10 of reactive protons in the catalytic system that facilitates efficient acid hydrolysis of recalcitrant  
11 cellulosic fibers. Moreover, a substantial build-up of in-vessel pressure by CO<sub>2</sub> release during the  
12 microwave-assisted reaction because of decomposition of PC or EC might have accelerated the  
13 conversion of paper towel wastes. PC and EC are prospective solvents for lignocellulosic biomass  
14 conversion considering their green features and notable catalytic performance, which have a good  
15 potential for substituting conventional organic solvents such as dimethylsulfoxide (DMSO) and  
16 tetrahydrofuran (THF) that are often considered hazardous in terms of health, safety, and  
17 environmental implications.

18 **Keywords:** Green solvent; propylene carbonate; ethylene carbonate; lignocellulose valorization;  
19 waste management; sustainable biorefinery.

20 **Graphical Abstract**

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24

25 **Synopsis**

26 This study promotes the sustainable conversion of lignocellulosic biomass waste in green solvents  
27 for the production of value-added chemicals.

## 28 Introduction

29 Lignocellulosic waste-based feedstock offers a sustainable alternative to diminishing petroleum-  
30 based resources considering environmental, economic, and political concerns. Considerable  
31 research interests have been directed towards the effective utilization of waste biomass for  
32 biorefinery applications in recent years<sup>1-3</sup>. Depolymerization is a crucial step to obtain sugars from  
33 lignocellulose which can be further upgraded to value-added chemicals and fuels in the biorefinery  
34 industry. It is essential to develop cost-effective technologies for lignocellulose depolymerization  
35 to achieve a high sugar yield using mild reaction conditions with low energy requirement<sup>4,5</sup>.

36 In this study, we propose paper towel waste as a potential waste-based feedstock for the production  
37 of sugars and chemicals. As the paper towel is a widely used sanitary product, a considerable  
38 amount of paper towel wastes is generated worldwide, which, for example, contributed to 5% of  
39 total waste generated at the Hong Kong International Airport. They are readily separated at source  
40 (e.g., commercial building, institutions), and hence easy to collect and transfer for potential  
41 valorization<sup>6</sup>. However, hygiene concerns and low biodegradability of highly cellulosic fibers  
42 make paper towel waste unsuitable for pulp recycling and biological treatment options, e.g.,  
43 anaerobic digestion and composting<sup>6,7</sup>. In this case, thermo-catalytic treatment can be an effective  
44 way for the sanitation and valorization of paper towel waste in a single process.

45 Depolymerization of cellulose-rich waste usually requires high reaction temperature or use of  
46 concentrated mineral acid due to the recalcitrant nature of highly crystalline cellulosic fibers,  
47 which can be detrimental to the environment<sup>4,8</sup>. The use of organic solvents can facilitate  
48 lignocellulose conversion under mild reaction conditions, such as dimethyl sulfoxide (DMSO),  
49 tetrahydrofuran (THF), and ionic liquids<sup>9-11</sup>. However, environmental and safety concerns have  
50 been raised against these conventional solvents, and their substitution with greener solvents is

51 recommended<sup>12,13</sup>. More research efforts are needed to explore green alternatives that are  
 52 environmentally benign without compromising the lignocellulose conversion efficiency<sup>14</sup>.  
 53 Recently, several studies have reported effective lignocellulose conversion using novel green  
 54 solvents such as  $\gamma$ -valerolactone (GVL)<sup>15-17</sup>.

55 Organic carbonate solvents, such as propylene carbonate (PC), ethylene carbonate (EC), and  
 56 dimethyl carbonate (DMC) exhibit high biodegradability, low toxicity, and good safety score  
 57 (stable under ambient conditions, low volatility, and flammability), while their synthesis involves  
 58 the utilization of carbon dioxide (CO<sub>2</sub>)<sup>12,18,19</sup> (Table 1). These environment-friendly features imply  
 59 their suitability as potential green solvents for biomass valorization. A few studies have reported  
 60 the improved rate of catalytic biomass conversion using PC<sup>15</sup>, EC<sup>20,21</sup>, and DMC<sup>22</sup> in the reaction  
 61 media. However, there is a lack of comparison among these carbonate solvents to understand their  
 62 potential roles in assisting catalytic depolymerization of lignocellulosic waste.

63 **Table 1:** Properties of organic carbonate solvents

Properties	PC	EC	DMC	Reference
Boiling point (°C)	242	248	90	12
Flash point (°C)	132	143	16	
Polarity	0.83	-	0.45	36
LD <sub>50</sub> (lethal dose) (oral) (rat) [mg kg <sup>-1</sup> ]	34920	>5000	9000	18
Biodegradability [d <sup>-1</sup> ]	94% (29)	readily	88% (28)	
Solubility with water [g L <sup>-1</sup> ] (20°C)	240	214	139	

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3 66 This study aims to investigate the use of PC, EC, and DMC as green co-solvents in a binary organic  
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5 67 solvent-water system for the conversion of paper towel waste catalyzed by dilute sulfuric acid  
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7 68 ( $\text{H}_2\text{SO}_4$ ) in mild reaction conditions. The study provides insights into the role of organic carbonate  
8  
9 69 solvents for the sustainable and efficient valorization of lignocellulosic feedstock in the  
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11 70 biorefinery.

## 15 71 **Experimental Section**

17 72 **Paper Towel Waste and Chemicals.** Paper towel wastes were collected from the Hong Kong  
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19 73 International airport (HKIA) and processed by drying ( $105^\circ\text{C}$ , 48 h) and blending (German Pool,  
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21 74 Pro-6). The paper towel wastes consist of 78.1% cellulose, 20.6% hemicellulose, and 1.3% lignin  
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23 75 as reported in our recent studies<sup>6</sup>. PC (99%), EC (99%), and DMC (99%) solvents were purchased  
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25 76 from Alfa Aesar. The standard chemical/compounds for calibration of the analytical equipment  
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27 77 and catalytic reaction included glucose (99%, UNI-chem, China); fructose ( $\geq 99\%$ ) and maltose  
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29 78 monohydrate (98%) from WAKO; levoglucosan from Fluorochem; levulinic acid (LA) (98%),  
30  
31 79 formic acid (FA) (98%), and cellobiose from Alfa Aesar; furfural (99%) and  
32  
33 80 hydroxymethylfurfural (HMF;  $\geq 99\%$ ) from Sigma Aldrich; and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%)  
34  
35 81 Honeywell Fluka. All standard chemicals were used as received without any alteration.

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39 82 **Catalytic Conversion.** The catalytic conversion of paper towel wastes was conducted in a  
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41 83 microwave reactor (Ethos Up Microwave Reactor, Milestone, maximum power of 1.9 kW) in  
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43 84 accordance with our previous studies<sup>6,15</sup>. To perform the catalytic test, the substrate (5 wt.%) was  
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45 85 loaded to a mixture of organic carbonate solvent (PC, EC, or DMC) and water (solvent mixture  
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47 86 ratio 1:1, total volume 10 ml); and 0.135 M  $\text{H}_2\text{SO}_4$  was used as the catalyst. Catalyst concentration  
48  
49 87 and solvent mixture ratio were employed following our previous studies<sup>6,16</sup>. The organic solvent-  
50  
51 88 water binary systems were denoted as PC/ $\text{H}_2\text{O}$ , EC/ $\text{H}_2\text{O}$ , and DMC/ $\text{H}_2\text{O}$ . The mixture of reactants  
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3 89 was placed in a Teflon vessel and sealed. It was subjected to heating to desired temperatures (120-  
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5 90 150°C) at a constant ramp rate (32°C min<sup>-1</sup>), followed by holding for 5-20 min. The in-vessel  
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7 91 reaction temperature and autogenous pressure were recorded using a standard thermocouple and  
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10 92 pressure data-logger, respectively in the microwave reactor. Apart from the mixed solvent systems,  
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12 93 catalytic conversion of paper towel wastes was also performed in pure water as a baseline for  
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14 94 comparison. To explore the role of carbonate solvents in depolymerization, paper towel waste was  
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16 95 treated in PC/H<sub>2</sub>O (140°C, 10 min) without acid addition and then oven-dried at 60°C overnight.  
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18 96 The dried substrate was subjected to microwave-assisted conversion in H<sub>2</sub>O (100%) (140°C, 10  
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20 97 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>). Control runs without paper towel waste were carried out in all solvent  
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22 98 systems at the same acid loading (0.135 M H<sub>2</sub>SO<sub>4</sub>) under selected reaction conditions.  
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26  
27 99 **Analysis of Samples.** Liquid samples were obtained from each replicate, diluted with deionized  
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29 100 water (DIW), and filtered through a 0.45 µm pore size membrane filter before analysis. In the case  
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31 101 of biphasic layers emerging after reactions in PC/H<sub>2</sub>O and DMC/H<sub>2</sub>O solvent systems, samples  
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33 102 were obtained from each layer for separate dilution in DIW and analysis. A water-insoluble top  
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35 103 layer appeared for PC/H<sub>2</sub>O solvent system at 150°C, which was dissolved firstly in ethanol and  
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37 104 subsequently diluted in DIW for sample preparation following the steps above. Soluble products  
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39 105 were analyzed by high-performance liquid chromatography (HPLC) using a Chromaster  
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41 106 instrument equipped with a refractive index detector (Hitachi, Japan). Sugars were quantified by  
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43 107 using an Agilent Hi-Plex Ca column and DIW (100%) as the mobile phase (0.4 ml min<sup>-1</sup>, 80°C),  
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45 108 after pH adjustment of samples (~7) by NaOH. Derivatives of sugars, including HMF, furfural,  
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47 109 FA, and LA, were quantified using an Aminex HPX-87H column (Bio-Rad), where 0.01 M H<sub>2</sub>SO<sub>4</sub>  
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50 110 was used as a mobile phase (0.5 ml min<sup>-1</sup>, 50°C). Standard compounds of known concentrations  
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3 111 were injected before sample analysis to ensure reliable calibration curves. The yield of sugars and  
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5 112 derivatives were calculated based on the carbon content (Eqn. (1))<sup>6,16</sup> of the paper towel waste.

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

10  
11  
12 114 Where  $\text{Conc}_p$  denotes the concentration of the products;  $\text{MW}_p$  and  $C_p$  represent the molecular mass  
13  
14 115 and mole number of carbons per mole of the product, respectively;  $C_s$  represents the total mole  
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16 116 number of carbons in cellulose (13.03 mmol) and hemicellulose fraction (3.44 mmol) of paper  
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18 117 towel (0.5 g) that is 16.47 mmol. A volume loss of 5-20% (at different temperatures) was recorded  
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21 118 for the binary solvent systems, which was taken into account for the product yield calculation.

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24 119 Post-reaction solid residues were collected through centrifugation followed by decantation. The  
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26 120 solids were washed with DIW for three times and oven-dried for 48 hours at 60°C and then ground  
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28 121 as a powder for characterization. Solid samples were characterized by X-ray diffraction (XRD)  
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30 122 (Rigaku Smatlab, 10° to 50° 2θ, rate: 10° min<sup>-1</sup> at 45 kV and 200 mA), scanning electron  
31  
32 123 microscope (SEM) (TESCAN VEGA3 XM), Brunauer–Emmett–Teller (BET) surface area  
33  
34 124 analyzer (Micromeritics ASAP 2020 Plus Version 1.02.01), and Fourier-transform infrared  
35  
36 125 spectroscopy (FTIR) (PerkinElmer, range: 4000cm<sup>-1</sup> to 400 cm<sup>-1</sup>, total 25 scans). The crystallinity  
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38 126 index ( $CrI$ ) was calculated from XRD patterns for untreated paper towel waste and post-reaction  
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42 127 solid residues according to the method reported in the literature<sup>6</sup>.

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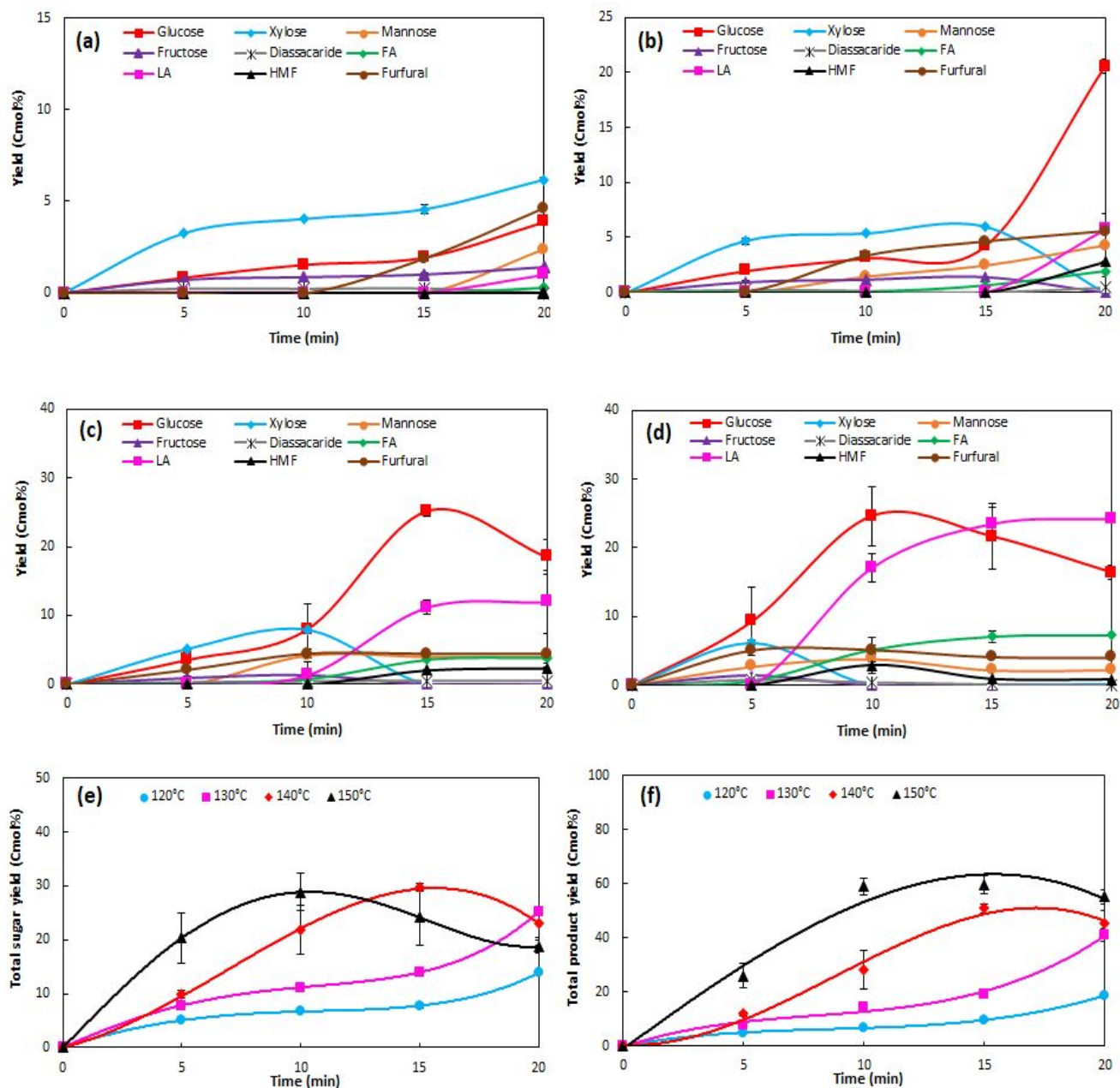
## 46 47 48 129 **Results and Discussion**

### 49 50 130 **Depolymerization of paper towel waste in PC/H<sub>2</sub>O solvent system.**

51  
52 131 Catalytic conversion of paper towel waste in PC/H<sub>2</sub>O showed relatively slow depolymerization at  
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54 132 120°C, achieving approximately 1-4 Cmol% of glucose, 3-6 Cmol% xylose, and 2 Cmol% of

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3 133 mannose during the 20-min reaction (Fig. 1a). The production of xylose and mannose were more  
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5 134 efficient than glucose, suggesting a lower energy requirement for the depolymerization of  
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7 135 hemicellulose compared to cellulose in PC/H<sub>2</sub>O. As the temperature increased to 130-150°C, a  
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10 136 sharp increase in the maximal glucose yield was observed (~21-25 Cmol%) in 10-20 min (Fig. 1b-  
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12 137 d), which is promising and comparable to glucose yield obtained in previous studies using  
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14 138 cellulosic substrate in the organic solvent-water system, for instance, ~10 Cmol% from vegetable  
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17 139 waste (DMSO/H<sub>2</sub>O, 120°C, 5 min, 0.5 g Amberlyst 36)<sup>10</sup>, ~20 Cmol% from paper towel waste  
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19 140 (GVL/H<sub>2</sub>O, 160°C, 5 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>)<sup>16</sup>, and ~14 Cmol% from Chinese Pennisetum  
20  
21 141 (GVL/H<sub>2</sub>O, 180°C, 20 min, 1 M H<sub>2</sub>SO<sub>4</sub>)<sup>17</sup>.

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23  
24 142 It is noted that the rate of glucose production increased at the point where the xylose yield started  
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26 143 to decline (fig. 1b-d). For instance, at 130°C, the glucose production rate was ~0.28 Cmol min<sup>-1</sup>  
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28 144 during 0-15 min of reaction while xylose yield was increasing. However, after 15 min, xylose yield  
29  
30 145 started to decline, and a rapid improvement in glucose production rate (~3.3 Cmol min<sup>-1</sup>) was  
31  
32 146 observed (Table 2). Cellulose fibers are usually covered by amorphous hemicellulose within  
33  
34 147 lignocellulosic biomass, which needs to be dissolved to improve the accessibility of cellulosic  
35  
36 148 fibers to protons in homogeneous catalytic condition<sup>23</sup>. A sharp increase in glucose yield in parallel  
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38 149 to the declining xylose yield might be because complete depolymerization of hemicellulose  
39  
40 150 exposed more cellulose fibers for favorable proton attack to facilitate cellulose hydrolysis.  
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42 151 Hemicellulose content is 21% of the total carbon in the paper towel waste, while the maximum  
43  
44 152 total yield of hemicellulosic monomers and derivatives (i.e., xylose, mannose, and furfural)  
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46 153 detected in PC/H<sub>2</sub>O was ~16.5 Cmol% (140°C, 10 min) (Fig. 1c), which indicates highly efficient  
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48 154 depolymerization of hemicellulose during the hydrolysis in the PC/H<sub>2</sub>O solvent.  
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156

157 **Fig. 1.** Product yields versus time during the catalytic conversion of paper towel waste in  
 158 PC/H<sub>2</sub>O solvent system at different temperatures (a) 120°C, (b) 130°C, (c) 140°C, (d) 150°C, (e)  
 159 total sugar yields at 120-150°C in PC/H<sub>2</sub>O, and (f) total product yields at 120-150°C in PC/H<sub>2</sub>O,  
 160 (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)

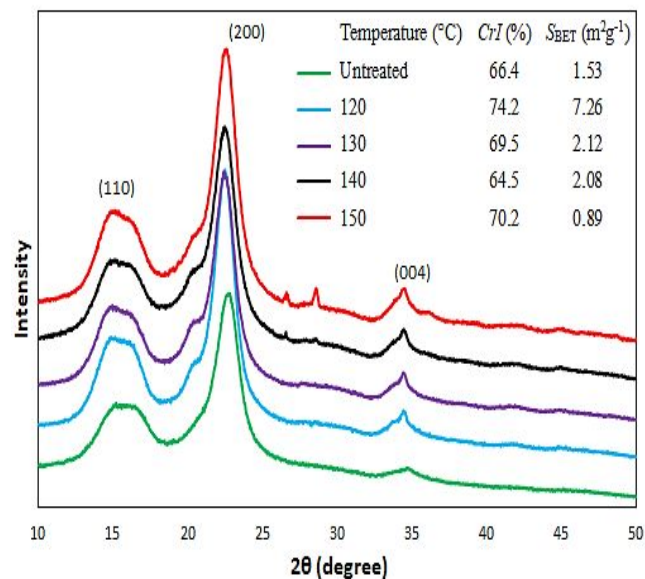
161

162 **Table 2:** Rate of glucose production in PC/H<sub>2</sub>O

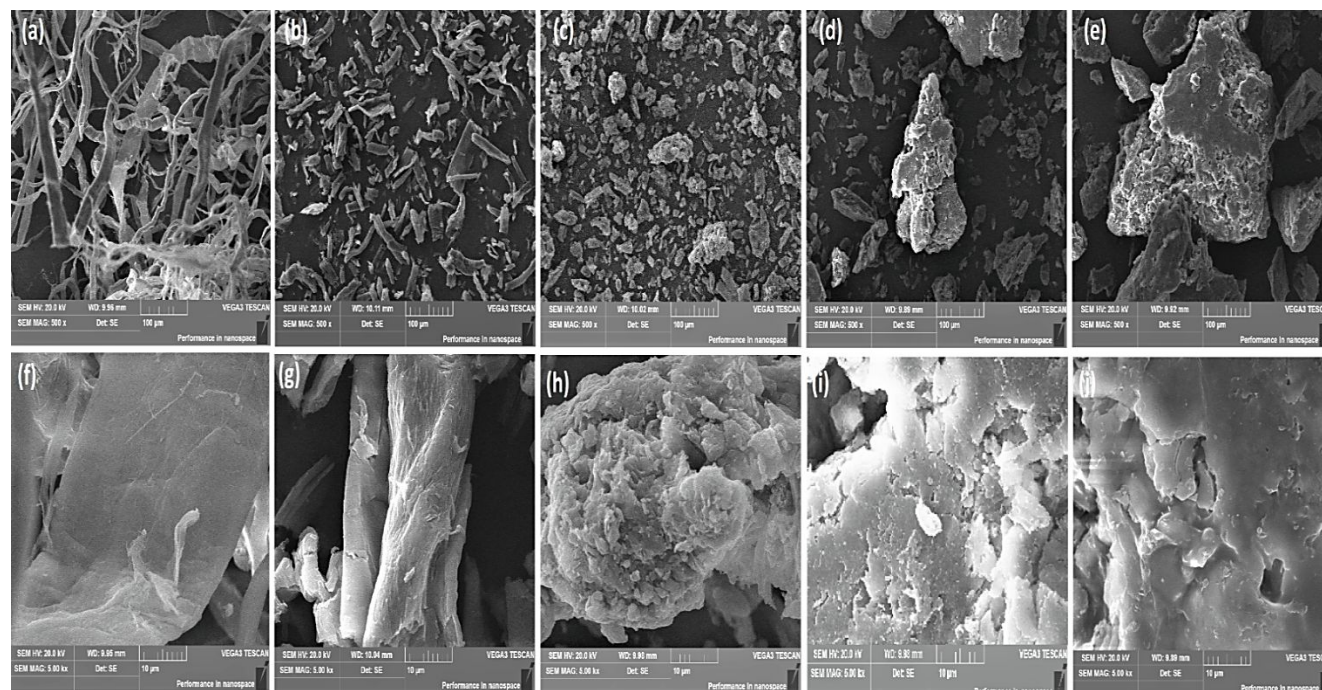
Temperature	Rate of glucose production (Cmol min <sup>-1</sup> )	
	Before declining xylose yield	After declining xylose yield
130°C	0.28	3.26
140°C	0.80	3.45
150°C	1.86	3.06

163  
164 The PC/H<sub>2</sub>O solvent system generated a maximum total sugar yield of ~30 Cmol% (140°C, 15  
165 min, and 150°C, 10 min) (Fig. 1e). A gradual decrease in total sugar yield was detected after 15  
166 min at 140°C and after 10 min at 150°C, indicating the secondary reactions of sugars, e.g.,  
167 dehydration to HMF and furfural and rehydration to LA. The negligible amount of fructose (~0.7-  
168 1.4 Cmol%) (Fig. 1a-d) suggests that glucose was converted to HMF via direct dehydration,  
169 without isomerization to fructose as the intermediate step. Strong Brønsted acids favor direct  
170 dehydration of glucose to HMF and have an insignificant effect on glucose-fructose  
171 isomerization<sup>10,24</sup>. The direct glucose dehydration was less feasible than that of xylose (to furfural),  
172 which is consistent with the previous findings<sup>25</sup> and plausibly suggests a lower energy barrier for  
173 the latter reaction. The maximum total soluble product yield achieved was ~60 Cmol% (150°C, 10  
174 min) (Fig. 1f), implying efficient depolymerization of paper towel waste in the PC/H<sub>2</sub>O solvent.

175 The crystallinity index (*CrI*) was calculated from the XRD patterns of post-reaction solid residues<sup>6</sup>  
176 in the PC/H<sub>2</sub>O solvent system (120-150°C, 20 min) (Fig. 2). The *CrI* increased from 66.4% for the  
177 untreated sample to 74.2% for residues obtained after heating at 120°C for 20 min, suggesting that  
178 most of the amorphous fraction was consumed for sugar production, and the proportion of  
179 crystalline fraction relatively increased. The small increase in BET surface area (7.26 m<sup>2</sup> g<sup>-1</sup> at  
180 120°C vs 1.53 m<sup>2</sup> g<sup>-1</sup> for untreated sample) possibly resulted from pores newly created along with  
181 the dissolution of the amorphous matrix. At higher temperatures, the crystalline fraction



182  
183 **Fig. 2.** XRD patterns, Crystallinity index (*CrI*) and BET surface area of untreated paper towel  
184 waste and post-reaction solid residue in PC/H<sub>2</sub>O solvent system at different temperatures 120°C,  
185 130°C, 140°C, and 150°C (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>,  
186 duration: 20 min, solvent ratio: 1:1)



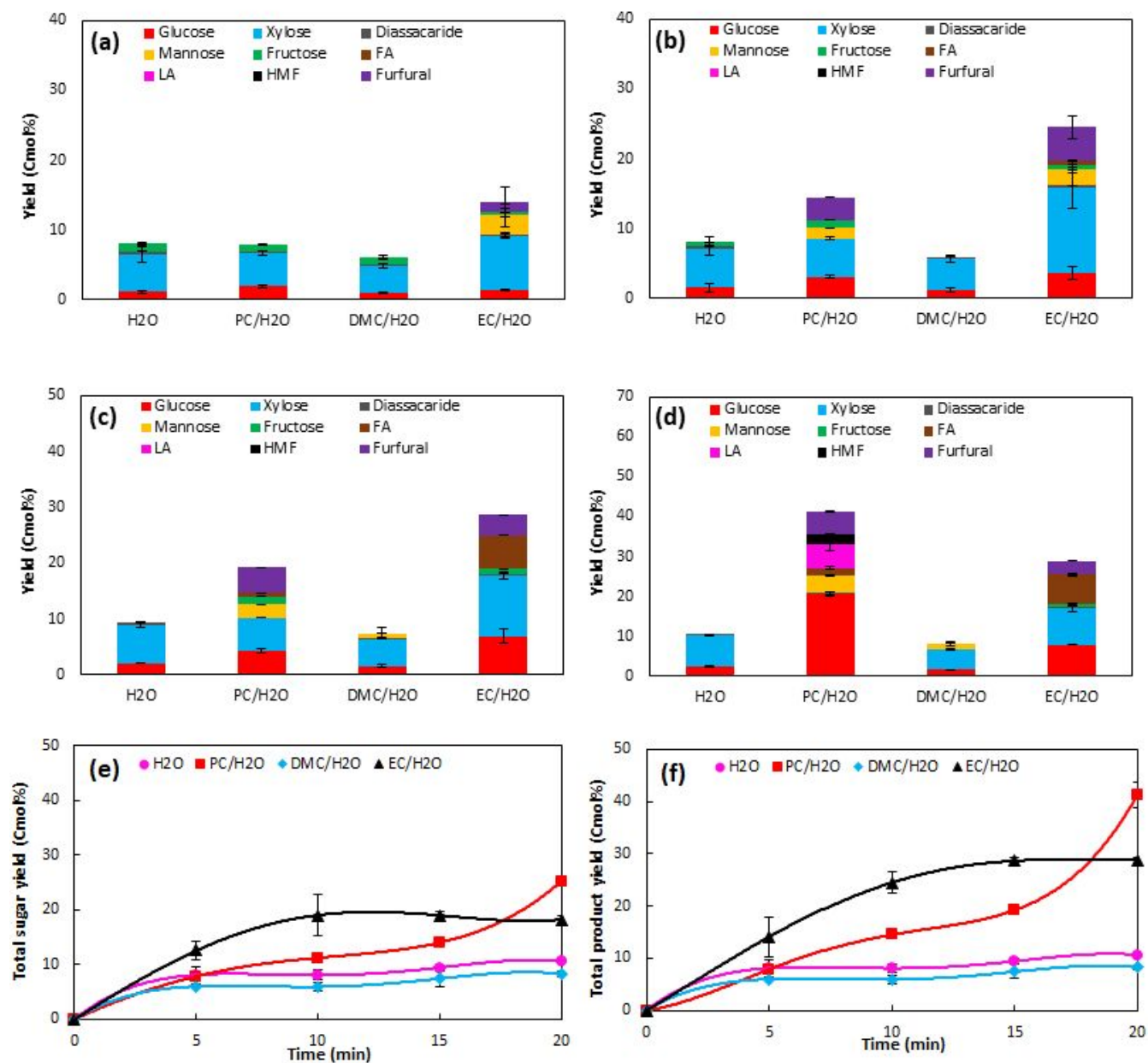
189 **Fig. 3.** Scanning electron microscope (SEM) images of untreated paper towel waste (a&f) and  
190 post-reaction solid residue in PC/H<sub>2</sub>O solvent system at different temperatures 120°C (b&g),  
191 130°C (c&h), 140°C (d&i), and 150°C (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j))  
192 magnification (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, duration: 20 min,  
193 solvent PC/H<sub>2</sub>O (1:1))

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3 194 decomposed given the decrease in *CrI* to 69.5% at 130°C and to 64.5% at 140°C. The SEM images  
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5 195 showed fiber breakdown with the increasing temperature in PC/H<sub>2</sub>O (Fig. 3).  
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### 8 196 **Comparative conversion in different carbonate solvent-water systems.**

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10 197 Among the solvents investigated, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O demonstrated enhanced depolymerization  
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12 198 of paper towel waste (total sugar yield up to ~25 Cmol% at 130°C) considering the conversion of  
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14 199 paper towel waste in 100% H<sub>2</sub>O as the baseline (total sugar up to ~11 Cmol%) (Fig. 4e). All  
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16 200 solvents generated similar glucose yield (~1-2 Cmol%) after 5 min of reaction at 130°C. Unlike  
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18 201 reaction in H<sub>2</sub>O only, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O demonstrated notable improvement in glucose yield  
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20 202 when the reaction was extended to 20 min (up to ~20 Cmol% in PC/H<sub>2</sub>O) (Fig. 4a-d). After 20-  
21  
22 203 min reaction (130°C), four times higher total soluble product yield (~41 Cmol%) was observed in  
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24 204 PC/H<sub>2</sub>O compared to that of H<sub>2</sub>O alone (~11 Cmol%) (Fig. 4f), demonstrating the effectiveness of  
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26 205 carbonate solvent system for the deconstruction of lignocellulosic fibers of paper towel waste.  
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28 206 Comparing the conversion in different carbonate solvent-water systems, EC/H<sub>2</sub>O was the most  
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30 207 efficient solvent in terms of total sugar yield (~19 Cmol%) and total product yield (~25 Cmol%)  
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32 208 at 130°C in 10 min (Fig. 4e, f). Apart from the improved glucose yield (~4 Cmol%), EC/H<sub>2</sub>O  
33  
34 209 generated a higher yield of xylose (~12 Cmol%) and mannose (~2.5 Cmol%) than other solvent  
35  
36 210 systems. Almost complete conversion of hemicellulose (i.e., 21% of the total carbon in the  
37  
38 211 substrate) was achieved in EC/H<sub>2</sub>O considering the total yield of xylose, mannose, and furfural  
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40 212 (~19.5 Cmol%) at 130°C in 10 min (Fig. 4b).  
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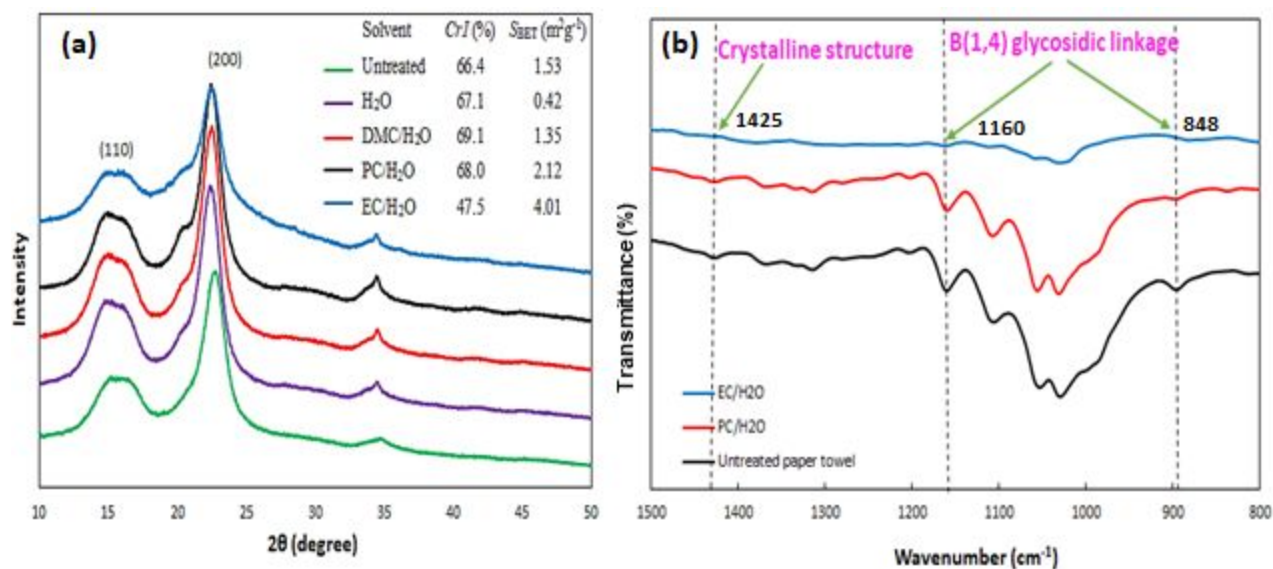
215 **Fig. 4.** Product yields during the catalytic conversion of paper towel waste in different solvent  
 216 systems subject to reaction duration- (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) total sugar  
 217 yields, and (f) total product yields (LA yield could not be quantified due to technical issue, and  
 218 total product yield in EC/H<sub>2</sub>O does not include the yield of LA) (Reaction condition: 5 wt%  
 219 substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, solvent ratio: 1:1)

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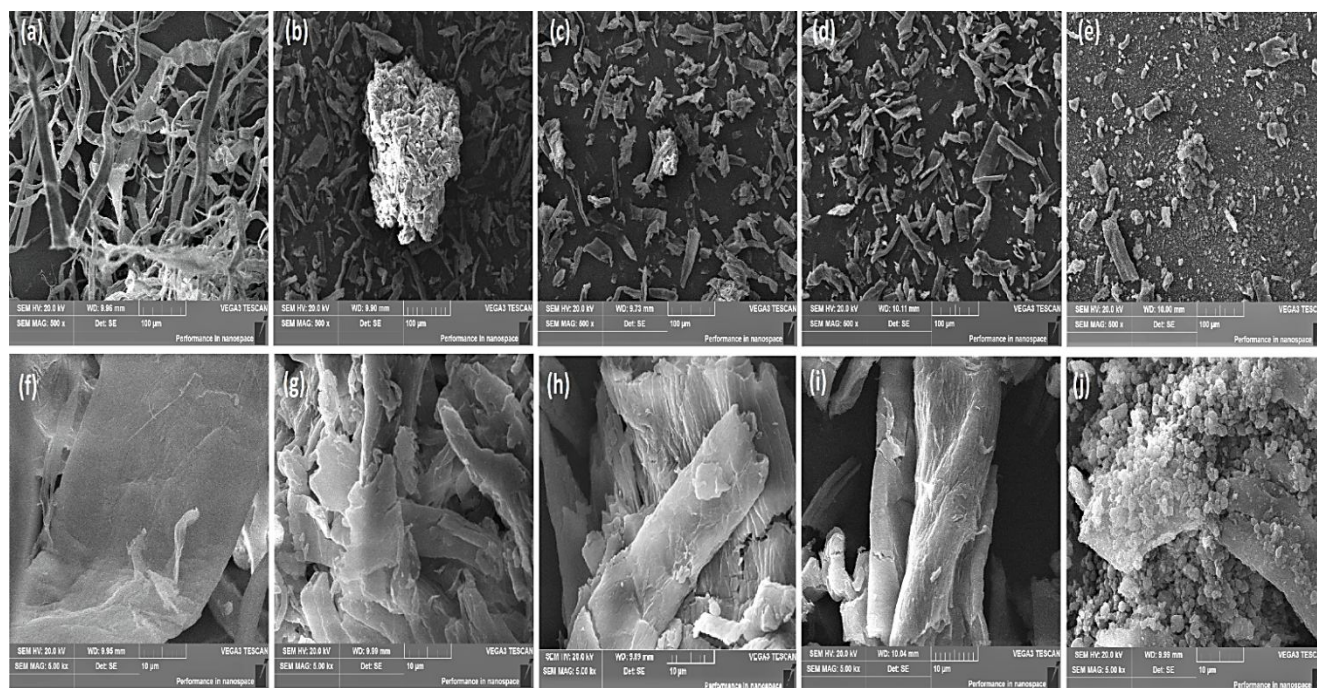
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3 222 Characterization of post-reaction solid residues indicated higher conversion of paper towel waste  
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5 223 in EC/H<sub>2</sub>O solvent compared to other solvents under the same reaction conditions. Calculated *CrI*  
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7 224 values of post-reaction solid residues (130°C, 20 min) (Fig. 5a) showed a slight increase in the  
8  
9 225 crystallinity ranging from ~67-69% for H<sub>2</sub>O (100%), PC/H<sub>2</sub>O, and DMC/H<sub>2</sub>O compared to  
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11 226 untreated paper towel waste (66.4%), possibly because the decomposition of the amorphous  
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13 227 fraction of cellulose led to a higher relative crystallinity<sup>10</sup>. In contrast, a substantial decrease in *CrI*  
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15 228 value (~47.5%) was observed in the EC/H<sub>2</sub>O system (Fig. 5a), which implies an efficient  
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17 229 breakdown of recalcitrant cellulosic fibers of paper towel. Similarly, SEM images revealed a  
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19 230 greater reduction in the fiber sizes (Fig. 6) in EC/H<sub>2</sub>O compared to other solvents. Moreover, an  
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21 231 increase in specific surface area ( $S_{\text{BET}}$  4.01 m<sup>2</sup>g<sup>-1</sup> at 130°C, 20 min) was measured for solid residue  
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23 232 in EC/H<sub>2</sub>O compared to untreated paper towel waste ( $S_{\text{BET}}$  1.53 m<sup>2</sup>g<sup>-1</sup>) and solid residues in other  
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25 233 solvent systems (Fig. 5a). Solid residues in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O were further analyzed through  
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27 234 FTIR (Fig. 5b), in which noticeable changes in transmittance were observed at 1425 cm<sup>-1</sup>, 1160  
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29 235 cm<sup>-1</sup>, and 848 cm<sup>-1</sup>. The observed peak at 1425 cm<sup>-1</sup> is associated with the crystalline structure of  
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31 236 cellulose<sup>26</sup>, which was reduced to a greater extent in EC/H<sub>2</sub>O compared to PC/H<sub>2</sub>O indicating a  
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33 237 significant alteration in the crystalline fraction of fibers. On the other hand, the observed peaks at  
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35 238 1160 cm<sup>-1</sup> and 848 cm<sup>-1</sup> can be attributed to C-O-C ring vibrational stretching of  $\beta(1,4)$  linkage of  
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37 239 cellulose<sup>27,28</sup>, which was also significantly altered in the solid residue in the EC/H<sub>2</sub>O solvent.  
38  
39 240 Analysis of soluble samples and characterization of solid residues consistently indicate a higher  
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41 241 conversion of paper towel waste in EC/H<sub>2</sub>O compared to other solvent systems in this study.  
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244 **Fig. 5.** (a) XRD patterns and (b) FTIR spectra of untreated paper towel waste and post-reaction  
 245 solid residue in different solvent systems (Reaction conditions: 5 wt% substrate loading,  
 246 temperature: 130°C, duration: 20 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)

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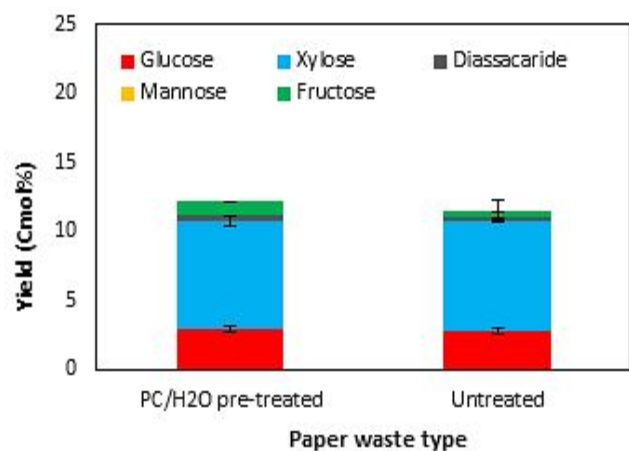
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250 **Fig. 6.** Scanning electron microscope (SEM) images of untreated paper towel waste (a&f) and  
 251 post-reaction solid residue in H<sub>2</sub>O (100%) (b&g), DMC/H<sub>2</sub>O (c&h), PC/H<sub>2</sub>O (d&i), and EC/H<sub>2</sub>O  
 252 (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j)) magnification (Reaction conditions: 5 wt%  
 253 substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, duration: 20 min, solvent ratio:1:1)

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3 **254 Role of carbonate solvents for effective depolymerization.**  
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5 255 Carbonate solvents might improve depolymerization through expansion and swelling of  
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7 256 lignocellulosic fibers or their participation in the catalytic process via activation of  
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10 257 protons/substrates, etc. To explore the potential roles of carbonate solvent, paper towel waste was  
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12 258 treated in PC/H<sub>2</sub>O (140°C, 10 min, no acid addition) and specific surface area of the treated  
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14 259 substrate was compared to that of untreated paper towel waste. Untreated and PC/H<sub>2</sub>O treated  
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16 260 paper towel waste showed similar  $S_{\text{BET}}$  values (1.03-1.5 m<sup>2</sup>g<sup>-1</sup>). Furthermore, PC/H<sub>2</sub>O treated paper  
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18 261 towel waste was subjected to the reaction in H<sub>2</sub>O (100%) (140°C, 10 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>). No  
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20 262 significant difference in the sugar yield was observed between untreated (~11 Cmol%) and solvent  
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22 263 treated (~12 Cmol%) substrate conversion (Fig. 7). These results suggest that carbonate solvents  
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25 264 on their own might not disrupt the structure or cause swelling of the paper towel waste. The  
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27 265 enhanced depolymerization of paper towel waste could be related to the higher activity of protons  
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29 266 in the presence of PC and EC as the aprotic solvents compared to that in water alone. The protons  
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31 267 from Brønsted acid catalyst tend to be more stabilized in H<sub>2</sub>O compared to a solvent system  
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33 268 containing an aprotic solvent due to the increased solvation of protons by H<sub>2</sub>O molecules, which  
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35 269 leads to the lower reactivity of Brønsted acid in H<sub>2</sub>O than that of an aprotic solvent<sup>29</sup>. Alternatively,  
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37 270 the organic solvent-water binary system can create a distinct phase near the surface of cellulose  
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39 271 through preferential binding of organic solvent molecules to the hydrophobic surface and binding  
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41 272 of water molecules with the hydrophilic surface. As a result, cellulose surfaces are chemically  
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43 273 modified and the induced bond cleavage can eventually enhance cellulose hydrolysis<sup>30,31</sup>.  
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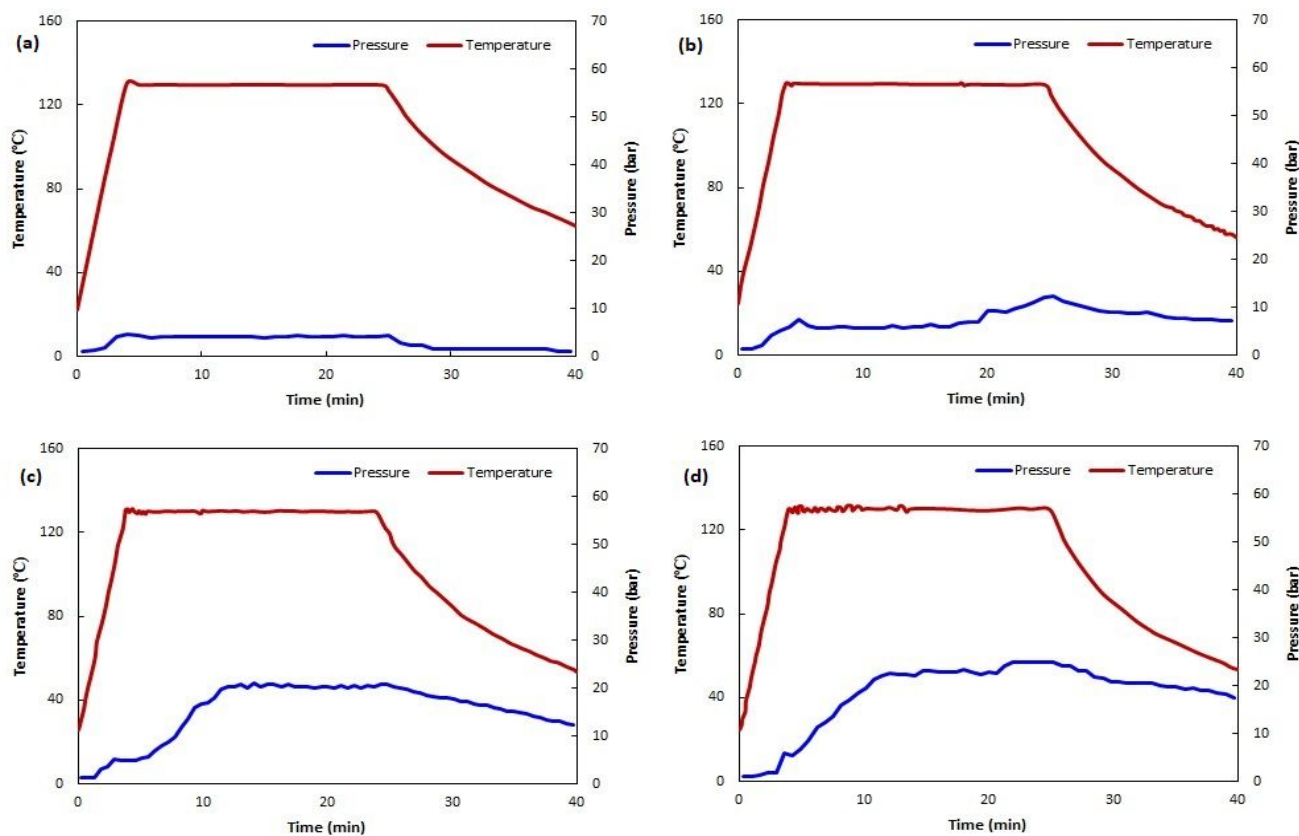
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**Fig. 7.** Sugar yields during the catalytic conversion of untreated and PC/H<sub>2</sub>O treated paper towel waste subject to the reaction in H<sub>2</sub>O (100%) (Reaction condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 140°C, duration: 10 min, solvent: H<sub>2</sub>O (100%))

Improved depolymerization of substrates in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvents could also be attributed to the significant in-vessel pressure development during catalytic conversion in these solvents, which reached up to ~26 bar (130°C, 20 min), in contrast to the maximum ~5 bar recorded for H<sub>2</sub>O only (Fig. 8). High *in situ* pressure during reaction has been reported to accelerate the conversion of lignocellulose in previous studies<sup>15,16,32</sup>. High in-vessel pressure development in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvent systems was associated with the release of CO<sub>2</sub> from solvent degradation as PC and EC could decompose to CO<sub>2</sub> and propylene and ethylene glycol, respectively, under the acidic condition<sup>15,33</sup>. A noticeable amount of gas bubbles was observed in the reacted solutions of PC/H<sub>2</sub>O and EC/H<sub>2</sub>O. At the same time, solvent loss of 5-20% was recorded depending on temperature and reaction duration, which suggests an irreversible production of CO<sub>2</sub> in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvent systems. An accelerated rate of acid-catalyzed reaction could be achieved when CO<sub>2</sub> was applied as an additive to reaction medium (high-temperature water), because the reaction between water and CO<sub>2</sub> produces carbonic acid that dissociates to increase the concentration of hydronium ion in the medium<sup>34,35</sup>. Nevertheless,

294 quantifying the catalytic effect of CO<sub>2</sub> generated due to carbonate solvent degradation is beyond  
 295 the scope of this study due to equipment and experimental limitations.



296  
 297 **Fig. 8.** In-vessel record of temperature and pressure during paper towel conversion (ramping and  
 298 reaction) in different solvents (a) H<sub>2</sub>O, (b) DMC/H<sub>2</sub>O, (c) PC/H<sub>2</sub>O, and (d) EC/H<sub>2</sub>O (Reaction  
 299 condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, duration: 20 min,  
 300 solvent ratio: 1:1)

301  
 302 Despite higher in-vessel pressure build-up during the reaction (~12 bar at 130°C, 20 min) (Fig. 8)  
 303 compared to H<sub>2</sub>O only, DMC/H<sub>2</sub>O unexpectedly generated a lower yield of sugars (~8 Cmol%  
 304 maximum) than that of H<sub>2</sub>O (~10 Cmol%). DMC has a lower polarity ( $\pi^*=0.45$ ) than H<sub>2</sub>O ( $\pi^*=$   
 305 1.09) and PC ( $\pi^*=0.83$ )<sup>36</sup>, which might influence the biomass conversion efficiency in DMC/H<sub>2</sub>O.  
 306 In low-polarity solvents, the catalytic activity could be hindered due to strong pairing between the  
 307 cation and anion, and active sites of the catalyst could be blocked by counter-ion. In contrast, the

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3 308 cation and anion are typically separated from each other in polar solvents, leading to high solvation  
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5 309 of ions that facilitate the catalytic activity, eliminating the interference of the counter-ion<sup>37</sup>. DMC  
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7 310 is considered as an effective methylation agent<sup>38,39</sup>. Methylation of starch and lignin in basic  
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9 311 conditions using DMC as the methylation agent has been reported in previous studies<sup>40,41</sup>.  
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11 312 Although little information exists regarding the reactions between cellulose (or its derivatives) and  
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13 313 DMC<sup>39</sup>, methylation of cellulose might occur to some extent under the given reaction conditions  
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15 314 in this study. This could contribute to the lower yield of sugars in DMC solvent; however, further  
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17 315 research is required to prove this postulation.  
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### 22 316 **Tandem dehydration-rehydration reactions in solvent systems.**

23  
24 317 A noticeable amount of sugar derivatives, i.e., HMF, LA, and FA were observed after 20 min of  
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26 318 reaction at 130°C and after 15 min at 140°C in PC/H<sub>2</sub>O (Fig. 1b, c), while furfural was detected at  
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28 319 a lower temperature (120°C, 15 min) (Fig. 1a) reflecting less energy-intensive dehydration of  
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30 320 xylose to furfural. At 150°C treatment in PC/H<sub>2</sub>O, LA yield (~23.5 Cmol%) surpassed glucose  
31  
32 321 yield (~21.6 Cmol%) after 15 min of reaction (Fig. 1d), suggesting that PC/H<sub>2</sub>O facilitated  
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34 322 dehydration-rehydration reactions of sugars in parallel to hydrolysis of paper towel waste.  
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36 323 Meanwhile, a decrease in the total detectable product yield in PC/H<sub>2</sub>O was observed at 140°C after  
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38 324 15 min and 150°C after 10 min (Fig. 1f). This indicates the formation of insoluble humins due to  
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40 325 polymerization between sugars and furan derivatives during the catalytic conversion of biomass at  
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42 326 a higher temperature<sup>11,42</sup>.  
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48 327 Comparing paper towel conversion at 130°C, no dehydration product was detected in the H<sub>2</sub>O  
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50 328 (100%) and DMC/H<sub>2</sub>O solvents; conversely, dehydration-rehydration products were detected in  
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52 329 the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvents starting from 10 min of reaction time (Fig. 4b). This suggests  
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54 330 the higher potential of PC and EC for tandem biomass hydrolysis and dehydration-rehydration  
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3 331 reactions. A notable LA yield (~6 Cmol%) generated in PC/H<sub>2</sub>O under mild reaction conditions  
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5 332 (130°C, 20 min) suggests that PC might be a preferable solvent for LA synthesis from  
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7 333 lignocellulosic biomass. The yield of LA could not be determined for EC/H<sub>2</sub>O solvent system due  
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9  
10 334 to technical issues (LA peak overlapped solvent peak). However, a substantial yield of FA (~6-7  
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12 335 Cmol% at 130°C, 15-20 min) was detected in the EC/H<sub>2</sub>O solvent, possibly inferring the yield of  
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14 336 LA in the solvent system as LA and FA are coproduced during the catalytic conversion of biomass  
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16  
17 337 and sugars<sup>10,43,44</sup>.

### 20 338 **Energy requirement for sugar production.**

21  
22 339 Energy requirement for sugar production was estimated and compared for different solvent  
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24 340 systems (Reaction conditions: 5 wt.% substrate loading, temperature: 130°C, duration: 10 min,  
25  
26 341 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1) based on the power consumption rate recorded in the  
27  
28 342 microwave reactor (Table 3). Energy requirement for ramping (up to 130°C at a ramp rate of 32°C  
29  
30 343 min<sup>-1</sup>) and reaction (holding at a constant temperature) were estimated separately and then added  
31  
32 344 up to determine the energy consumption per unit of sugar produced in different solvent systems.  
33  
34 345 The results revealed a lower energy requirement (~0.03 kWh) at the ramping stage for carbonate  
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36 346 solvent-water binary systems, in contrast, H<sub>2</sub>O only required relatively higher energy (~0.05 kWh)  
37  
38 347 for heating up the reaction mixture. Furthermore, binary solvents exhibited a lower energy  
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40 348 consumption per unit of sugar production (Table 3) than that of H<sub>2</sub>O, as low as 0.002 kWh mol<sup>-1</sup>  
41  
42 349 in EC/H<sub>2</sub>O, which was the most efficient solvent system in terms of energy requirement for sugar  
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45 350 production from paper towel waste.

50 351

352 **Table 3:** Energy consumption for sugar production in different solvent systems

Solvent	Energy consumption (kWh)			Sugar produced (mol) (per 5 g of paper towel)	Energy consumption per unit of sugar production (kWh mol <sup>-1</sup> )
	Ramp	Reaction	Total		
PC/H <sub>2</sub> O	0.034	0.036	0.071	11.19	0.006
EC/H <sub>2</sub> O	0.033	0.007	0.040	18.98	0.002
DMC/H <sub>2</sub> O	0.037	0.035	0.073	5.91	0.012
H <sub>2</sub> O	0.05	0.062	0.110	8.04	0.014

353 (Reaction conditions: 5 wt% substrate loading, temperature: 130°C, duration: 10 min, 0.135 M  
 354 H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)  
 355

356 **Conclusions**

357 The investigated organic carbonate binary solvents, i.e., PC/H<sub>2</sub>O and EC/H<sub>2</sub>O, effectively  
 358 facilitated the depolymerization of lignocellulosic paper towel waste under mild reaction  
 359 conditions. This study explored the potential roles of carbonate solvents in the catalytic system.  
 360 Higher availability of reactive protons in these solvent systems and autogenous pressure  
 361 development might favor the breakdown of cellulosic fibers compared to H<sub>2</sub>O only. Besides, a  
 362 considerable amount of sugar derivatives was detected in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O (at a higher  
 363 temperature and longer duration), suggesting the suitability of solvents for tandem hydrolysis and  
 364 dehydration of biomass. The study implies that PC and EC have a high potential to be considered  
 365 as greener alternatives to commonly used industrial solvents for the efficient valorization of  
 366 biomass. However, these solvents have a high boiling point (242-248°C), which can be challenging  
 367 for product separation and solvent recovery by distillation. Future research efforts can be directed  
 368 to address this issue by selective adsorption for possible implementation of these alternative  
 369 solvents on an industrial scale.

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3 371 **Note.** The authors declare no conflict of interest.  
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9 373 **Acknowledgement**  
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