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Complete List of Authors:	Dutta, Shanta; The Hong Kong Polytechnic University, Department of Civil and Environmental Engineering Yu, Iris KM; Technische Universität München Fakultät für Chemie, Lehrstuhl für Technische Chemie II Tsang, Daniel; The Hong Kong Polytechnic University, Department of Civil and Environmental Engineering Fan, Jiajun; University of York, Chemistry Clark, James Hanley; University of York, Chemistry Jiang, Zhicheng; Sichuan University, Su, Zhishan; Sichuan University, College of Chemistry Hu, Changwei; Sichuan University, College of Chemistry Poon, C.S.; The Hong Kong Polytechnic University, Department of Civil and Environmental Engineering

Efficient Depolymerization of Cellulosic Paper Towel Waste Using Organic Carbonate Solvents

Shanta Dutta[a], Iris K.M. Yu[a,b], Daniel C.W. Tsang[a,*], Jiajun Fan[c], James H. Clark[c], Zhicheng Jiang[d], Zhishan Su[e], Changwei Hu[e], Chi Sun Poon[a]

[a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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

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

[d] Department of Biomass Science and Engineering, Sichuan University, Chengdu, Sichuan 610064, China

[e] Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

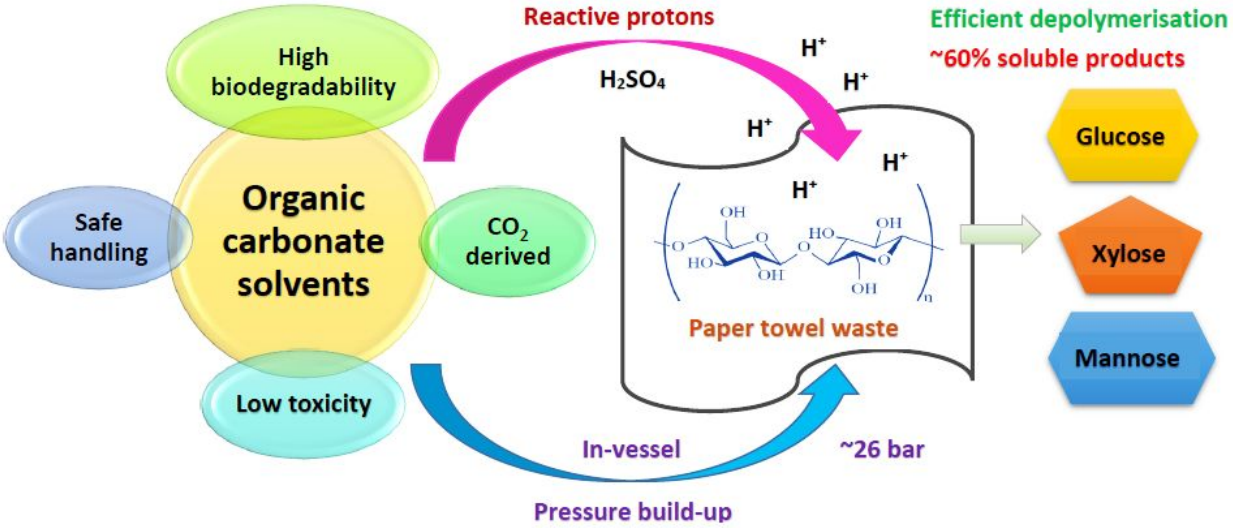
*Corresponding author, dan.tsang@polyu.edu.hk

Abstract

Efficient depolymerization of lignocellulosic biomass is a prerequisite for sugar production and its subsequent up-gradation to fuels and chemicals. Organic carbonate solvents, i.e., propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC), which are low in toxicity and biodegradable, were investigated as 'green' co-solvents (PC/H_2O, EC/H_2O, DMC/H_2O, solvent ratio 1:1) for depolymerization of cellulosic paper towel waste. PC/H_2O and EC/H_2O enhanced the depolymerization of paper towel waste and improved the total sugar yield (up to ~25 Cmol%) compared to H_2O only (up to ~11 Cmol%) at mild reaction conditions (130°C, 20 min). The higher performance of PC/H_2O and EC/H_2O can be attributed to higher availability of reactive protons in the catalytic system that facilitates efficient acid hydrolysis of recalcitrant cellulosic fibers. Moreover, a substantial build-up of in-vessel pressure by CO_2 release during the microwave-assisted reaction because of decomposition of PC or EC might have accelerated the conversion of paper towel wastes. PC and EC are prospective solvents for lignocellulosic biomass conversion considering their green features and notable catalytic performance, which have a good potential for substituting conventional organic solvents such as dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) that are often considered hazardous in terms of health, safety, and environmental implications.

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

Graphical Abstract



Synopsis

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

Introduction

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

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

Depolymerization of cellulose-rich waste usually requires high reaction temperature or use of concentrated mineral acid due to the recalcitrant nature of highly crystalline cellulosic fibers, which can be detrimental to the environment[4,8]. The use of organic solvents can facilitate lignocellulose conversion under mild reaction conditions, such as dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and ionic liquids[9-11]. However, environmental and safety concerns have been raised against these conventional solvents, and their substitution with greener solvents is recommended[12,13]. More research efforts are needed to explore green alternatives that are environmentally benign without compromising the lignocellulose conversion efficiency[14]. Recently, several studies have reported effective lignocellulose conversion using novel green solvents such as γ-valerolactone (GVL)[15-17].

Organic carbonate solvents, such as propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC) exhibit high biodegradability, low toxicity, and good safety score (stable under ambient conditions, low volatility, and flammability), while their synthesis involves the utilization of carbon dioxide (CO_2)[12,18,19] (Table 1). These environment-friendly features imply their suitability as potential green solvents for biomass valorization. A few studies have reported the improved rate of catalytic biomass conversion using PC[15], EC[20,21], and DMC[22] in the reaction media. However, there is a lack of comparison among these carbonate solvents to understand their potential roles in assisting catalytic depolymerization of lignocellulosic waste.

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_{50} (lethal dose) (oral) (rat) [mg kg^{-1}]	34920	>5000	9000	18
Biodegradability [d^{-1}]	94% (29)	readily	88% (28)	
Solubility with water [g L^{-1}] (20°C)	240	214	139	

This study aims to investigate the use of PC, EC, and DMC as green co-solvents in a binary organic solvent-water system for the conversion of paper towel waste catalyzed by dilute sulfuric acid (H_2SO_4) in mild reaction conditions. The study provides insights into the role of organic carbonate solvents for the sustainable and efficient valorization of lignocellulosic feedstock in the biorefinery.

Experimental Section

Paper Towel Waste and Chemicals. Paper towel wastes were collected from the Hong Kong International airport (HKIA) and processed by drying (105°C, 48 h) and blending (German Pool, Pro-6). The paper towel wastes consist of 78.1% cellulose, 20.6% hemicellulose, and 1.3% lignin as reported in our recent studies[6]. PC (99%), EC (99%), and DMC (99%) solvents were purchased from Alfa Aesar. The standard chemical/compounds for calibration of the analytical equipment and catalytic reaction included glucose (99%, UNI-chem, China); fructose (≥99%) and maltose monohydrate (98%) from WAKO; levoglucosan from Fluorochem; levulinic acid (LA) (98%), formic acid (FA) (98%), and cellobiose from Alfa Aesar; furfural (99%) and hydroxymethylfurfural (HMF; ≥99%) from Sigma Aldrich; and sulfuric acid (H_2SO_4, 98%) Honeywell Fluka. All standard chemicals were used as received without any alteration.

Catalytic Conversion. The catalytic conversion of paper towel wastes was conducted in a microwave reactor (Ethos Up Microwave Reactor, Milestone, maximum power of 1.9 kW) in accordance with our previous studies[6,15]. To perform the catalytic test, the substrate (5 wt.%) was loaded to a mixture of organic carbonate solvent (PC, EC, or DMC) and water (solvent mixture ratio 1:1, total volume 10 ml); and 0.135 M H_2SO_4 was used as the catalyst. Catalyst concentration and solvent mixture ratio were employed following our previous studies[6,16]. The organic solvent-water binary systems were denoted as PC/H_2O, EC/H_2O, and DMC/H_2O. The mixture of reactants was placed in a Teflon vessel and sealed. It was subjected to heating to desired temperatures (120-150°C) at a constant ramp rate (32°C min^{-1}), followed by holding for 5-20 min. The in-vessel reaction temperature and autogenous pressure were recorded using a standard thermocouple and pressure data-logger, respectively in the microwave reactor. Apart from the mixed solvent systems, catalytic conversion of paper towel wastes was also performed in pure water as a baseline for comparison. To explore the role of carbonate solvents in depolymerization, paper towel waste was treated in PC/H_2O (140°C, 10 min) without acid addition and then oven-dried at 60°C overnight. The dried substrate was subjected to microwave-assisted conversion in H_2O (100%) (140°C, 10 min, 0.135 M H_2SO_4). Control runs without paper towel waste were carried out in all solvent systems at the same acid loading (0.135 M H_2SO_4) under selected reaction conditions.

Analysis of Samples. Liquid samples were obtained from each replicate, diluted with deionized water (DIW), and filtered through a 0.45 μm pore size membrane filter before analysis. In the case of biphasic layers emerging after reactions in PC/H_2O and DMC/H_2O solvent systems, samples were obtained from each layer for separate dilution in DIW and analysis. A water-insoluble top layer appeared for PC/H_2O solvent system at 150°C, which was dissolved firstly in ethanol and subsequently diluted in DIW for sample preparation following the steps above. Soluble products were analyzed by high-performance liquid chromatography (HPLC) using a Chromaster instrument equipped with a refractive index detector (Hitachi, Japan). Sugars were quantified by using an Agilent Hi-Plex Ca column and DIW (100%) as the mobile phase (0.4 ml min^{-1}, 80°C), after pH adjustment of samples (~7) by NaOH. Derivatives of sugars, including HMF, furfural, FA, and LA, were quantified using an Aminex HPX-87H column (Bio-Rad), where 0.01 M H_2SO_4 was used as a mobile phase (0.5 ml min^{-1}, 50°C). Standard compounds of known concentrations were injected before sample analysis to ensure reliable calibration curves. The yield of sugars and derivatives were calculated based on the carbon content (Eqn. (1))[6,16] of the paper towel waste.

$$Product\ yield\ (Cmol\%) = \frac{Conc_p\ (mg\ ml^{-1}) \times Vol\ (ml)/MW_p \times C_p}{C_s\ (mol)} \times 100 \qquad (1)$$

Where $Conc_p$ denotes the concentration of the products; MW_p and C_p represent the molecular mass and mole number of carbons per mole of the product, respectively; C_s represents the total mole number of carbons in cellulose (13.03 mmol) and hemicellulose fraction (3.44 mmol) of paper towel (0.5 g) that is 16.47 mmol. A volume loss of 5-20% (at different temperatures) was recorded for the binary solvent systems, which was taken into account for the product yield calculation.

Post-reaction solid residues were collected through centrifugation followed by decantation. The solids were washed with DIW for three times and oven-dried for 48 hours at 60°C and then ground as a powder for characterization. Solid samples were characterized by X-ray diffraction (XRD) (Rigaku Smatlab, 10° to 50° 2θ, rate: 10° min^{-1} at 45 kV and 200 mA), scanning electron microscope (SEM) (TESCAN VEGA3 XM), Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics ASAP 2020 Plus Version 1.02.01), and Fourier-transform infrared spectroscopy (FTIR) (PerkinElmer, range: 4000cm^{-1} to 400 cm^{-1}, total 25 scans). The crystallinity index (*CrI*) was calculated from XRD patterns for untreated paper towel waste and post-reaction solid residues according to the method reported in the literature[6].

Results and Discussion

Depolymerization of paper towel waste in PC/H_2O solvent system.

Catalytic conversion of paper towel waste in PC/H_2O showed relatively slow depolymerization at 120°C, achieving approximately 1-4 Cmol% of glucose, 3-6 Cmol% xylose, and 2 Cmol% of mannose during the 20-min reaction (Fig. 1a). The production of xylose and mannose were more efficient than glucose, suggesting a lower energy requirement for the depolymerization of hemicellulose compared to cellulose in PC/H_2O. As the temperature increased to 130-150°C, a sharp increase in the maximal glucose yield was observed (~21-25 Cmol%) in 10-20 min (Fig. 1b-d), which is promising and comparable to glucose yield obtained in previous studies using cellulosic substrate in the organic solvent-water system, for instance, ~10 Cmol% from vegetable waste (DMSO/H_2O, 120°C, 5 min, 0.5 g Amberlyst 36)[10], ~20 Cmol% from paper towel waste (GVL/H_2O, 160°C, 5 min, 0.135 M H_2SO_4)[16], and ~14 Cmol% from Chinese Pennisetum (GVL/H_2O, 180°C, 20 min, 1 M H_2SO_4)[17].

It is noted that the rate of glucose production increased at the point where the xylose yield started to decline (fig. 1b-d). For instance, at 130°C, the glucose production rate was ~0.28 Cmol min^{-1} during 0-15 min of reaction while xylose yield was increasing. However, after 15 min, xylose yield started to decline, and a rapid improvement in glucose production rate (~3.3 Cmol min^{-1}) was observed (Table 2). Cellulose fibers are usually covered by amorphous hemicellulose within lignocellulosic biomass, which needs to be dissolved to improve the accessibility of cellulosic fibers to protons in homogeneous catalytic condition[23]. A sharp increase in glucose yield in parallel to the declining xylose yield might be because complete depolymerization of hemicellulose exposed more cellulose fibers for favorable proton attack to facilitate cellulose hydrolysis. Hemicellulose content is 21% of the total carbon in the paper towel waste, while the maximum total yield of hemicellulosic monomers and derivatives (i.e., xylose, mannose, and furfural) detected in PC/H_2O was ~16.5 Cmol% (140°C, 10 min) (Fig. 1c), which indicates highly efficient depolymerization of hemicellulose during the hydrolysis in the PC/H_2O solvent.

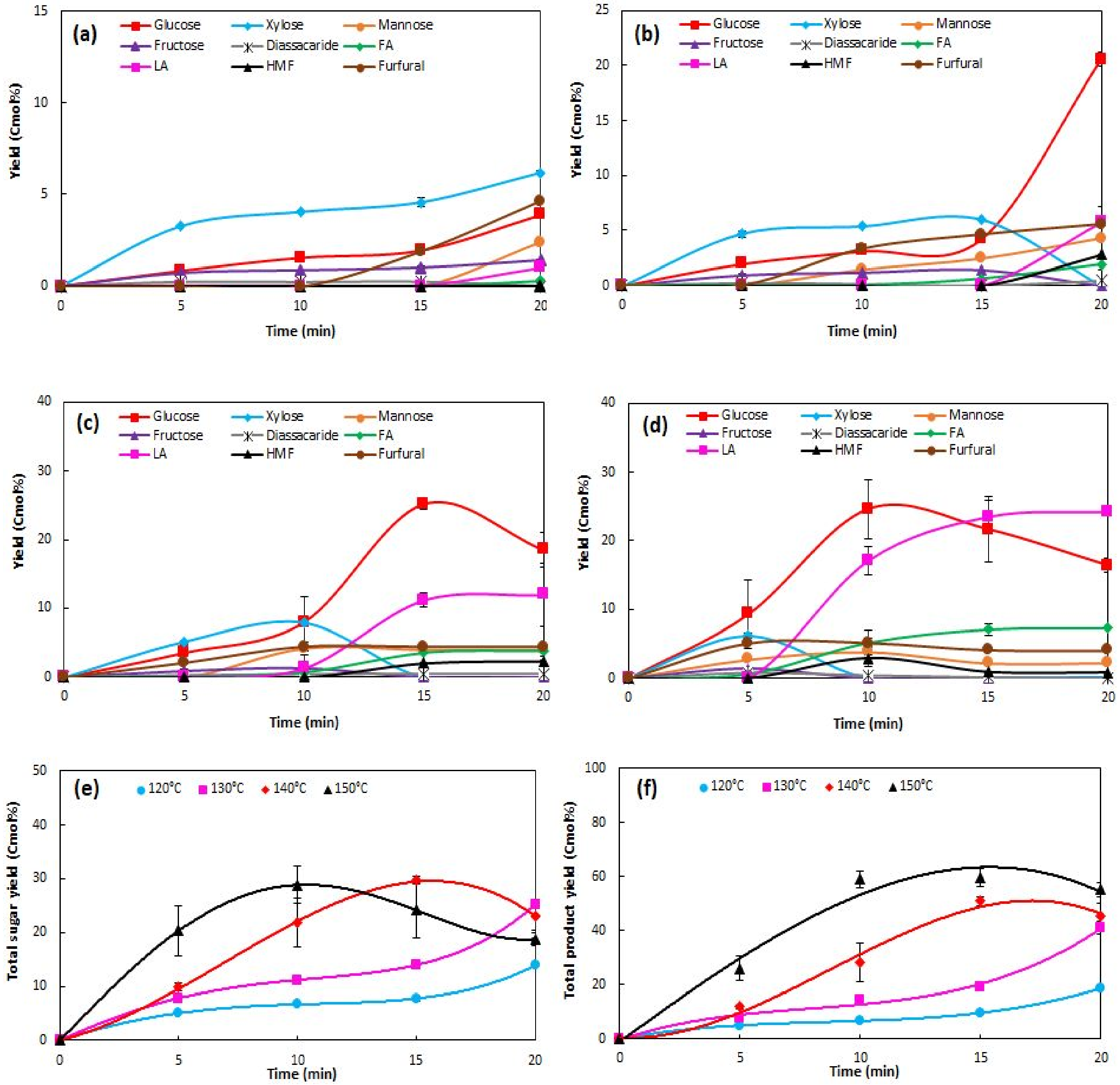


Fig. 1. Product yields versus time during the catalytic conversion of paper towel waste in PC/H_2O solvent system at different temperatures (a) 120°C, (b) 130°C, (c) 140°C, (d) 150°C, (e) total sugar yields at 120-150°C in PC/H_2O, and (f) total product yields at 120-150°C in PC/H_2O, (Reaction conditions: 5 wt% substrate loading, 0.135 M H_2SO_4, solvent ratio: 1:1)

Table 2: Rate of glucose production in PC/H_2O

	Rate of glucose production (Cmol min^{-1})	
Temperature	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

The PC/H_2O solvent system generated a maximum total sugar yield of ~30 Cmol% (140°C, 15 min, and 150°C, 10 min) (Fig. 1e). A gradual decrease in total sugar yield was detected after 15 min at 140°C and after 10 min at 150°C, indicating the secondary reactions of sugars, e.g., dehydration to HMF and furfural and rehydration to LA. The negligible amount of fructose (~0.7-1.4 Cmol%) (Fig. 1a-d) suggests that glucose was converted to HMF via direct dehydration, without isomerization to fructose as the intermediate step. Strong Brønsted acids favor direct dehydration of glucose to HMF and have an insignificant effect on glucose-fructose isomerization[10,24]. The direct glucose dehydration was less feasible than that of xylose (to furfural), which is consistent with the previous findings[25] and plausibly suggests a lower energy barrier for the latter reaction. The maximum total soluble product yield achieved was ~60 Cmol% (150°C, 10 min) (Fig. 1f), implying efficient depolymerization of paper towel waste in the PC/H_2O solvent.

The crystallinity index (*CrI*) was calculated from the XRD patterns of post-reaction solid residues[6] in the PC/H_2O solvent system (120-150°C, 20 min) (Fig. 2). The *CrI* increased from 66.4% for the untreated sample to 74.2% for residues obtained after heating at 120°C for 20 min, suggesting that most of the amorphous fraction was consumed for sugar production, and the proportion of crystalline fraction relatively increased. The small increase in BET surface area (7.26 m^2 g^{-1} at 120^{o}C vs 1.53 m^2 g^{-1} for untreated sample) possibly resulted from pores newly created along with the dissolution of the amorphous matrix. At higher temperatures, the crystalline fraction

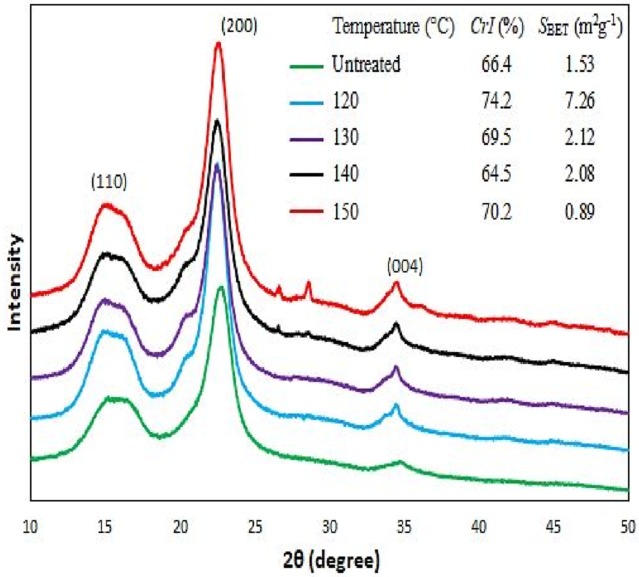


Fig. 2. XRD patterns, Crystallinity index (*CrI*) and BET surface area of untreated paper towel waste and post-reaction solid residue in PC/H_2O solvent system at different temperatures 120°C, 130°C, 140°C, and 150°C (Reaction conditions: 5 wt% substrate loading, 0.135 M H_2SO_4, duration: 20 min, solvent ratio: 1:1)

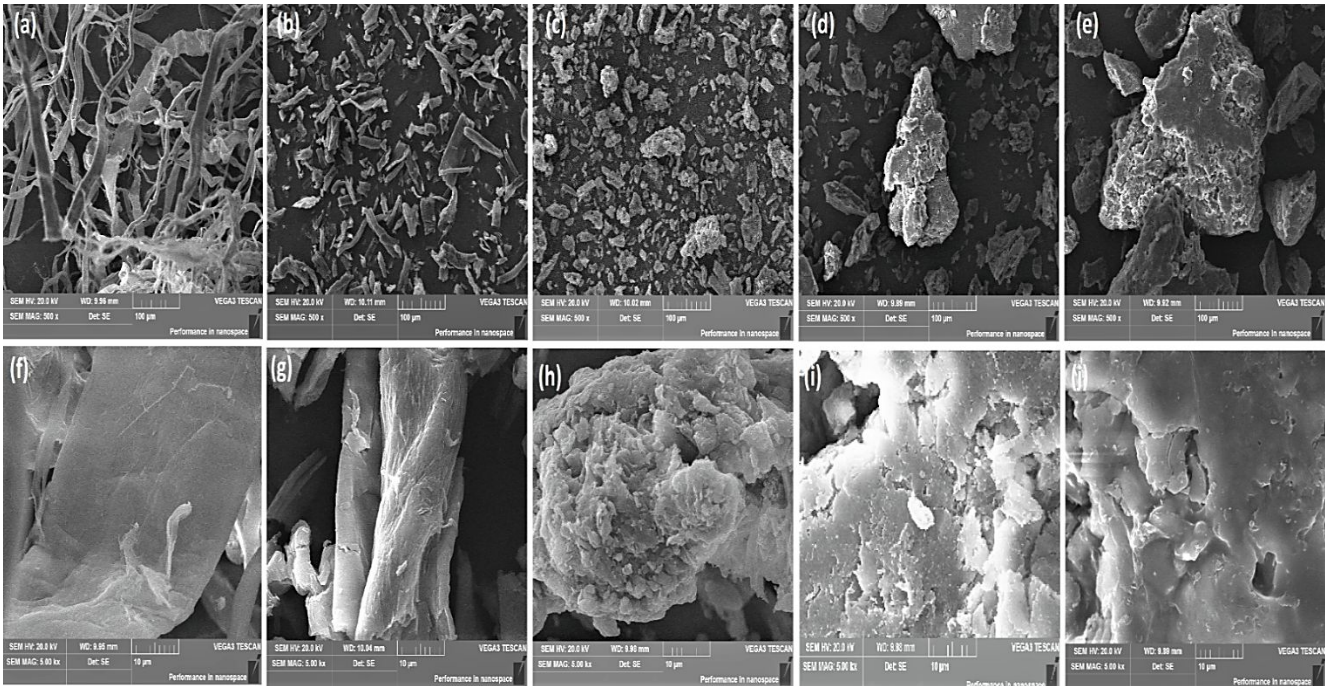


Fig. 3. Scanning electron microscope **(**SEM) images of untreated paper towel waste (a&f) and post-reaction solid residue in PC/H_2O solvent system at different temperatures 120°C (b&g), 130°C (c&h), 140°C (d&i), and 150°C (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j)) magnification (Reaction conditions: 5 wt% substrate loading, 0.135 M H_2SO_4, duration: 20 min, solvent PC/H_2O (1:1))

decomposed given the decrease in *CrI* to 69.5% at 130°C and to 64.5% at 140°C. The SEM images showed fiber breakdown with the increasing temperature in PC/H_2O (Fig. 3).

Comparative conversion in different carbonate solvent-water systems.

Among the solvents investigated, PC/H_2O and EC/H_2O demonstrated enhanced depolymerization of paper towel waste (total sugar yield up to ~25 Cmol% at 130°C) considering the conversion of paper towel waste in 100% H_2O as the baseline (total sugar up to ~11 Cmol%) (Fig. 4e). All solvents generated similar glucose yield (~1-2 Cmol%) after 5 min of reaction at 130°C. Unlike reaction in H_2O only, PC/H_2O and EC/H_2O demonstrated notable improvement in glucose yield when the reaction was extended to 20 min (up to ~20 Cmol% in PC/H_2O) (Fig. 4a-d). After 20-min reaction (130°C), four times higher total soluble product yield (~41 Cmol%) was observed in PC/H_2O compared to that of H_2O alone (~11 Cmol%) (Fig. 4f), demonstrating the effectiveness of carbonate solvent system for the deconstruction of lignocellulosic fibers of paper towel waste. Comparing the conversion in different carbonate solvent-water systems, EC/H_2O was the most efficient solvent in terms of total sugar yield (~19 Cmol%) and total product yield (~25 Cmol%) at 130°C in 10 min (Fig. 4e, f). Apart from the improved glucose yield (~4 Cmol%), EC/H_2O generated a higher yield of xylose (~12 Cmol%) and mannose (~2.5 Cmol%) than other solvent systems. Almost complete conversion of hemicellulose (i.e., 21% of the total carbon in the substrate) was achieved in EC/H_2O considering the total yield of xylose, mannose, and furfural (~19.5 Cmol%) at 130°C in 10 min (Fig. 4b).

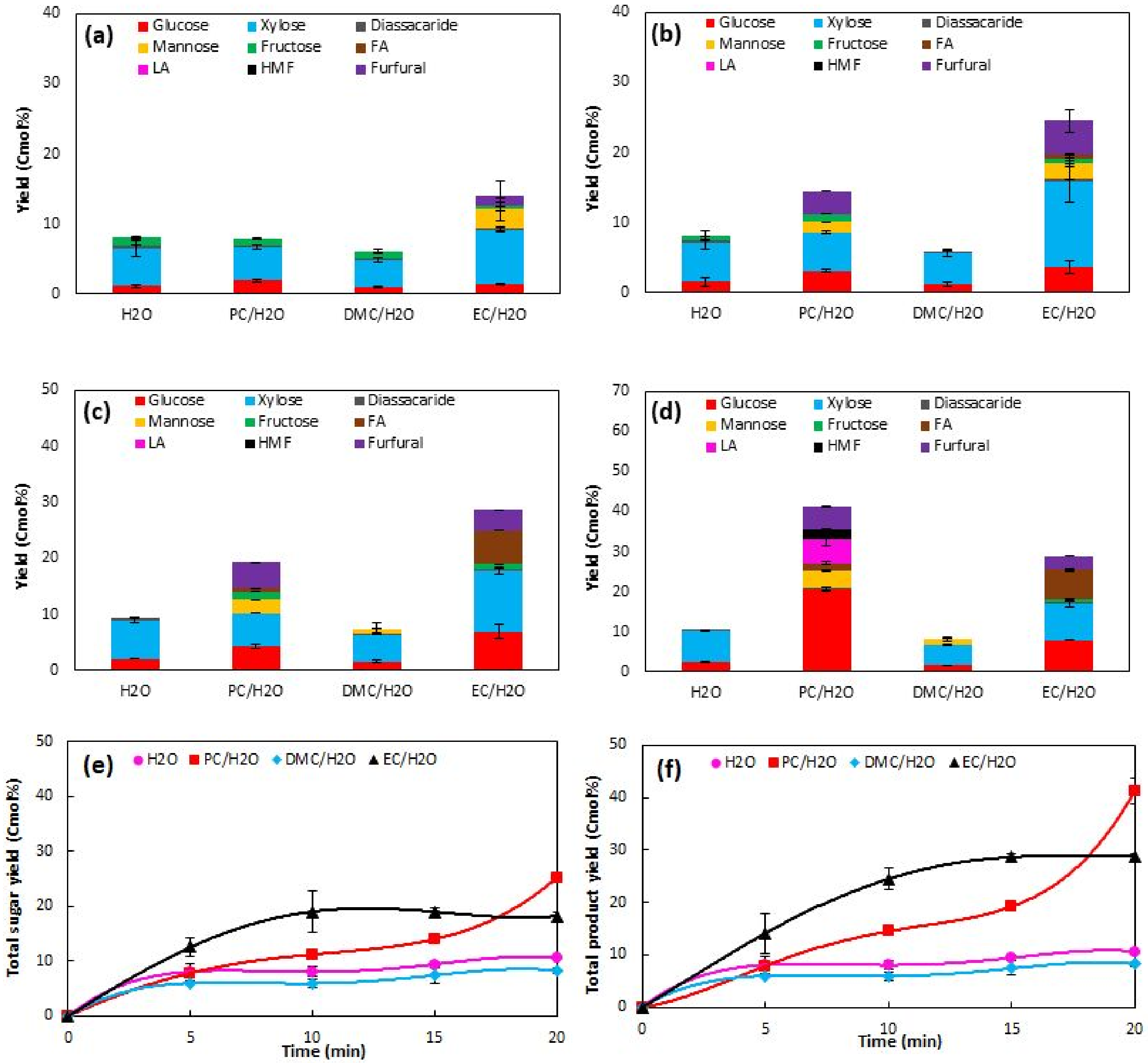


Fig. 4. Product yields during the catalytic conversion of paper towel waste in different solvent systems subject to reaction duration- (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) total sugar yields, and (f) total product yields (LA yield could not be quantified due to technical issue, and total product yield in EC/H_2O does not include the yield of LA) (Reaction condition: 5 wt% substrate loading, 0.135 M H_2SO_4, temperature: 130°C, solvent ratio: 1:1)

Characterization of post-reaction solid residues indicated higher conversion of paper towel waste in EC/H_2O solvent compared to other solvents under the same reaction conditions. Calculated *CrI* values of post-reaction solid residues (130°C, 20 min) (Fig. 5a) showed a slight increase in the crystallinity ranging from ~67-69% for H_2O (100%), PC/H_2O, and DMC/H_2O compared to untreated paper towel waste (66.4%), possibly because the decomposition of the amorphous fraction of cellulose led to a higher relative crystallinity[10]. In contrast, a substantial decrease in *CrI* value (~47.5%) was observed in the EC/H_2O system (Fig. 5a), which implies an efficient breakdown of recalcitrant cellulosic fibers of paper towel. Similarly, SEM images revealed a greater reduction in the fiber sizes (Fig. 6) in EC/H_2O compared to other solvents. Moreover, an increase in specific surface area (S_{BET} 4.01 m^2g^{-1} at 130°C, 20 min) was measured for solid residue in EC/H_2O compared to untreated paper towel waste (S_{BET} 1.53 m^2g^{-1}) and solid residues in other solvent systems (Fig. 5a). Solid residues in PC/H_2O and EC/H_2O were further analyzed through FTIR (Fig. 5b), in which noticeable changes in transmittance were observed at 1425 cm^{-1}, 1160 cm^{-1}, and 848 cm^{-1}. The observed peak at 1425 cm^{-1} is associated with the crystalline structure of cellulose[26], which was reduced to a greater extent in EC/H_2O compared to PC/H_2O indicating a significant alteration in the crystalline fraction of fibers. On the other hand, the observed peaks at 1160 cm^{-1} and 848 cm^{-1} can be attributed to C-O-C ring vibrational stretching of β(1,4) linkage of cellulose[27,28], which was also significantly altered in the solid residue in the EC/H_2O solvent. Analysis of soluble samples and characterization of solid residues consistently indicate a higher conversion of paper towel waste in EC/H_2O compared to other solvent systems in this study.

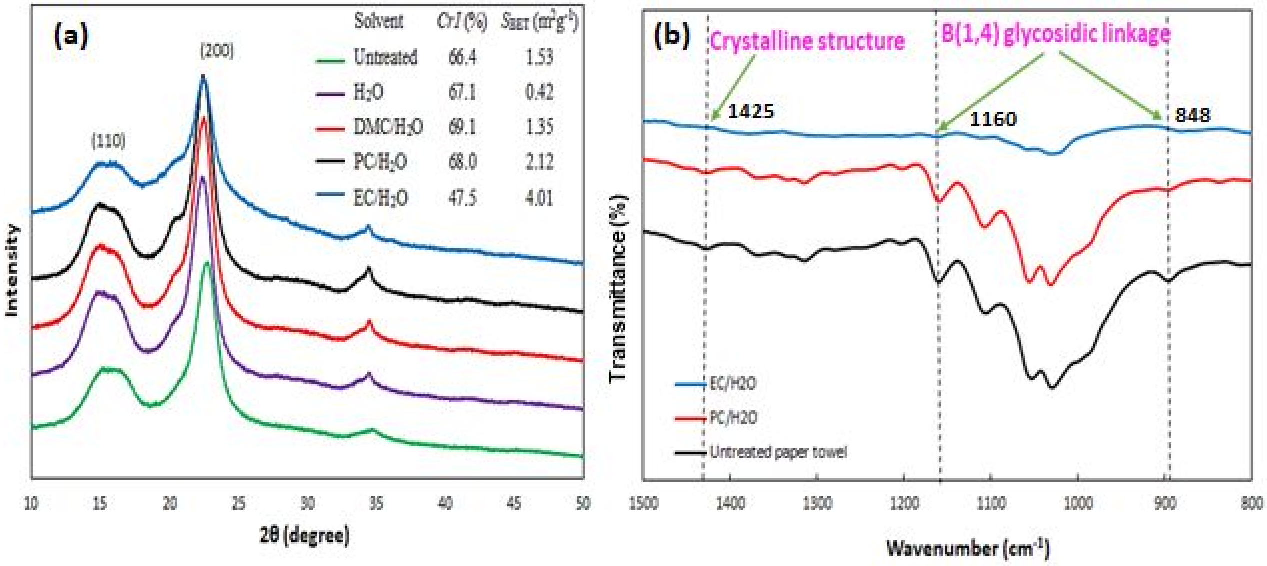


Fig. 5. (a) XRD patterns and (b) FTIR spectra of untreated paper towel waste and post-reaction solid residue in different solvent systems (Reaction conditions: 5 wt% substrate loading, temperature: 130°C, duration: 20 min, 0.135 M H_2SO_4, solvent ratio: 1:1)

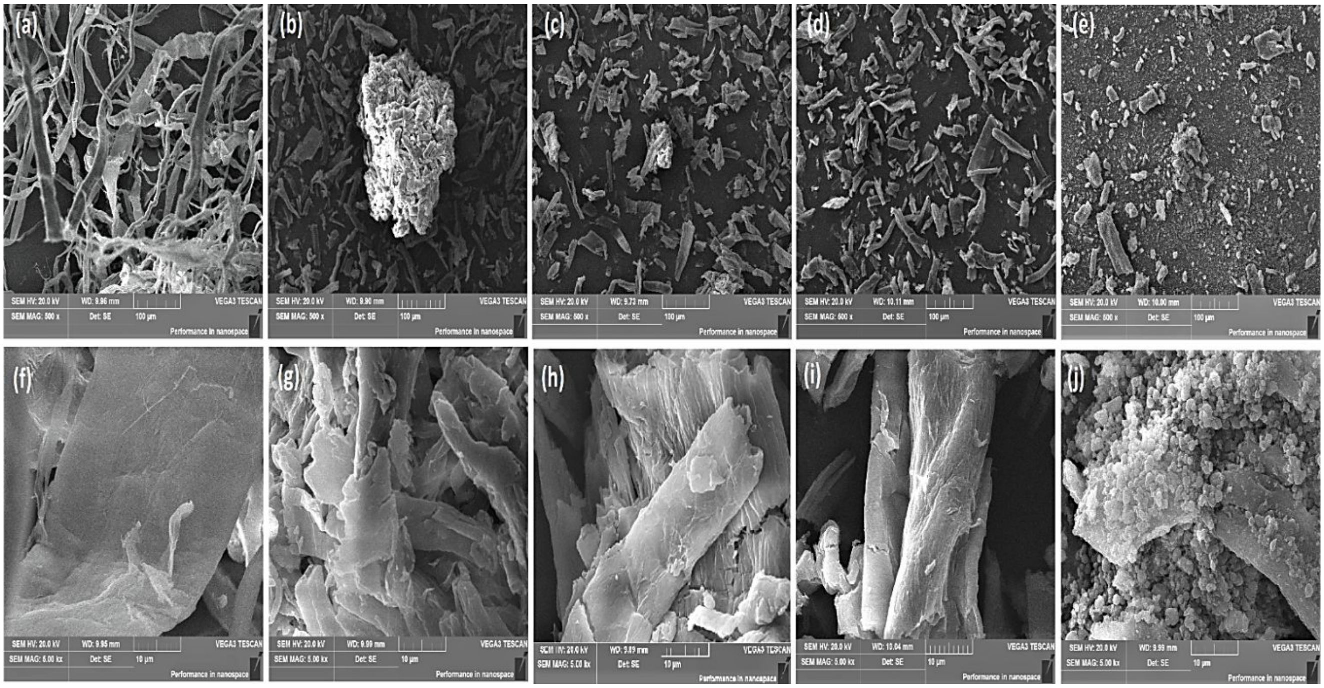


Fig. 6. Scanning electron microscope (SEM) images of untreated paper towel waste (a&f) and post-reaction solid residue in H_2O (100%) (b&g), DMC/H_2O (c&h), PC/H_2O (d&i), and EC/H_2O (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j)) magnification (Reaction conditions: 5 wt% substrate loading, 0.135 M H_2SO_4, temperature: 130°C, duration: 20 min, solvent ratio:1:1)

Role of carbonate solvents for effective depolymerization.

Carbonate solvents might improve depolymerization through expansion and swelling of lignocellulosic fibers or their participation in the catalytic process via activation of protons/substrates, etc. To explore the potential roles of carbonate solvent, paper towel waste was treated in PC/H_2O (140°C, 10 min, no acid addition) and specific surface area of the treated substrate was compared to that of untreated paper towel waste. Untreated and PC/H_2O treated paper towel waste showed similar S_{BET} values (1.03-1.5 m^2g^{-1}). Furthermore, PC/H_2O treated paper towel waste was subjected to the reaction in H_2O (100%) (140°C, 10 min, 0.135 M H_2SO_4). No significant difference in the sugar yield was observed between untreated (~11 Cmol%) and solvent treated (~12 Cmol%) substrate conversion (Fig. 7). These results suggest that carbonate solvents on their own might not disrupt the structure or cause swelling of the paper towel waste. The enhanced depolymerization of paper towel waste could be related to the higher activity of protons in the presence of PC and EC as the aprotic solvents compared to that in water alone. The protons from BrØnsted acid catalyst tend to be more stabilized in H_2O compared to a solvent system containing an aprotic solvent due to the increased solvation of protons by H_2O molecules, which leads to the lower reactivity of BrØnsted acid in H_2O than that of an aprotic solvent[29]. Alternatively, the organic solvent-water binary system can create a distinct phase near the surface of cellulose through preferential binding of organic solvent molecules to the hydrophobic surface and binding of water molecules with the hydrophilic surface. As a result, cellulose surfaces are chemically modified and the induced bond cleavage can eventually enhance cellulose hydrolysis[30,31].

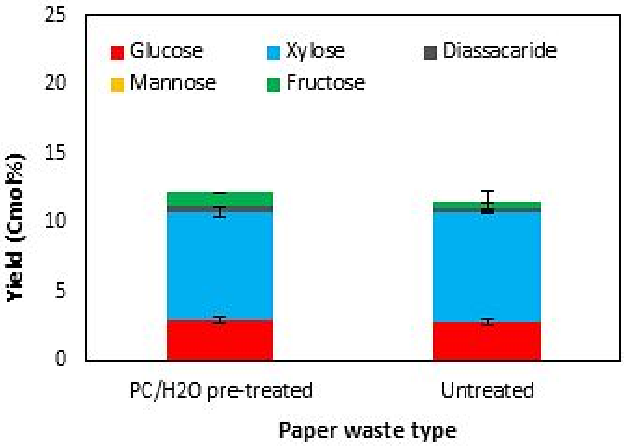


Fig. 7. Sugar yields during the catalytic conversion of untreated and PC/H2O treated paper towel waste subject to the reaction in H2O (100%) (Reaction condition: 5 wt% substrate loading, 0.135 M H2SO4, temperature: 140°C, duration: 10 min, solvent: H2O (100%))

Improved depolymerization of substrates in the PC/H_2O and EC/H_2O 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_2O only (Fig. 8). High *in situ* pressure during reaction has been reported to accelerate the conversion of lignocellulose in previous studies[15,16,32]. High in-vessel pressure development in the PC/H_2O and EC/H_2O solvent systems was associated with the release of CO_2 from solvent degradation as PC and EC could decompose to CO_2 and propylene and ethylene glycol, respectively, under the acidic condition[15,33]. A noticeable amount of gas bubbles was observed in the reacted solutions of PC/H_2O and EC/H_2O. At the same time, solvent loss of 5-20% was recorded depending on temperature and reaction duration, which suggests an irreversible production of CO_2 in the PC/H_2O and EC/H_2O solvent systems. An accelerated rate of acid-catalyzed reaction could be achieved when CO_2 was applied as an additive to reaction medium (high-temperature water), because the reaction between water and CO_2 produces carbonic acid that dissociates to increase the concentration of hydronium ion in the medium[34,35]. Nevertheless, quantifying the catalytic effect of CO_2 generated due to carbonate solvent degradation is beyond the scope of this study due to equipment and experimental limitations.

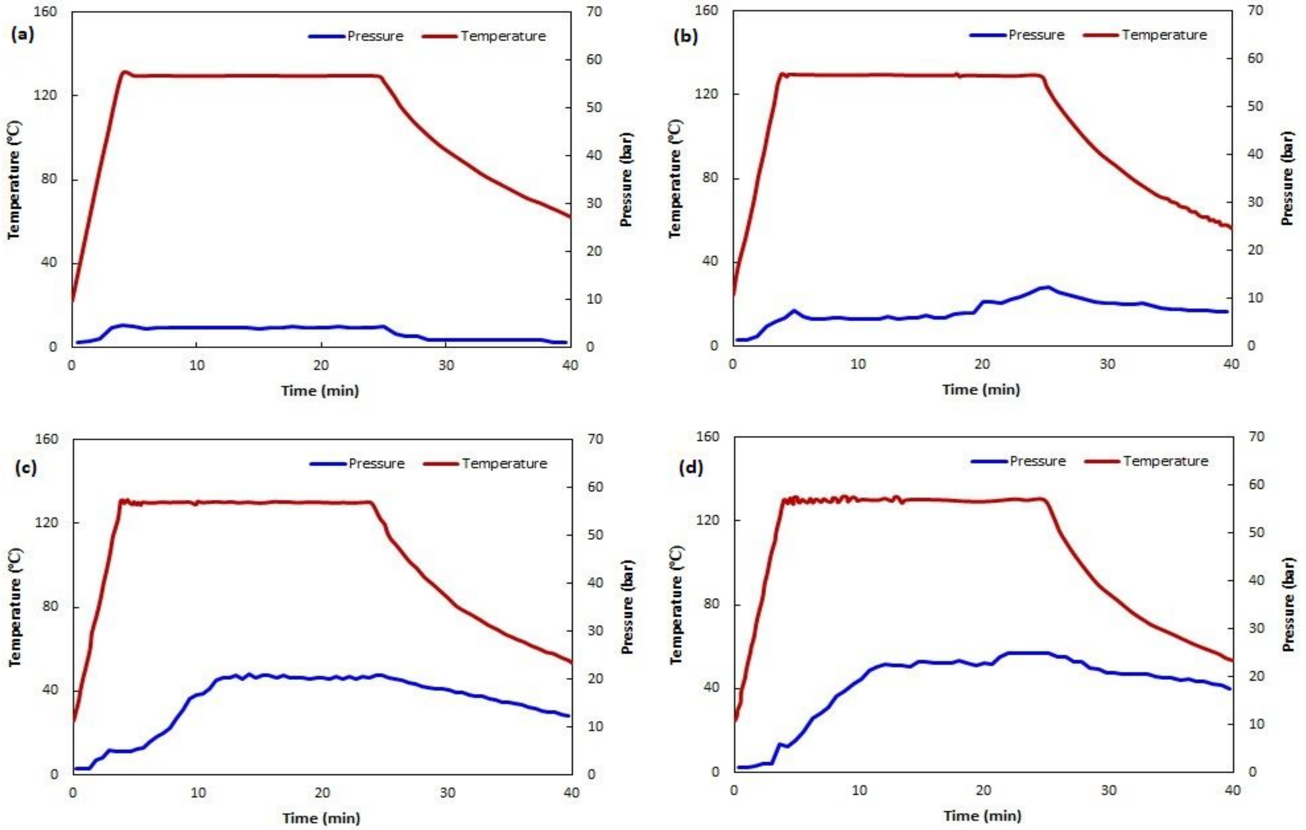


Fig. 8. In-vessel record of temperature and pressure during paper towel conversion (ramping and reaction) in different solvents (a) H_2O, (b) DMC/H_2O, (c) PC/H_2O, and (d) EC/H_2O (Reaction condition: 5 wt% substrate loading, 0.135 M H_2SO_4, temperature: 130°C, duration: 20 min, solvent ratio: 1:1)

Despite higher in-vessel pressure build-up during the reaction (~12 bar at 130°C, 20 min) (Fig. 8) compared to H_2O only, DMC/H_2O unexpectedly generated a lower yield of sugars (~8 Cmol% maximum) than that of H_2O (~10 Cmol%). DMC has a lower polarity (π^*= 0.45) than H_2O (π^*= 1.09) and PC (π^*=0.83)[36], which might influence the biomass conversion efficiency in DMC/H_2O. In low-polarity solvents, the catalytic activity could be hindered due to strong pairing between the cation and anion, and active sites of the catalyst could be blocked by counter-ion. In contrast, the cation and anion are typically separated from each other in polar solvents, leading to high solvation of ions that facilitate the catalytic activity, eliminating the interference of the counter-ion[37]. DMC is considered as an effective methylation agent[38,39]. Methylation of starch and lignin in basic conditions using DMC as the methylation agent has been reported in previous studies[40,41]. Although little information exists regarding the reactions between cellulose (or its derivatives) and DMC[39], methylation of cellulose might occur to some extent under the given reaction conditions in this study. This could contribute to the lower yield of sugars in DMC solvent; however, further research is required to prove this postulation.

Tandem dehydration-rehydration reactions in solvent systems.

A noticeable amount of sugar derivatives, i.e., HMF, LA, and FA were observed after 20 min of reaction at 130°C and after 15 min at 140°C in PC/H_2O (Fig. 1b, c), while furfural was detected at a lower temperature (120°C, 15 min) (Fig. 1a) reflecting less energy-intensive dehydration of xylose to furfural. At 150°C treatment in PC/H_2O, LA yield (~23.5 Cmol%) surpassed glucose yield (~21.6 Cmol%) after 15 min of reaction (Fig. 1d), suggesting that PC/H_2O facilitated dehydration-rehydration reactions of sugars in parallel to hydrolysis of paper towel waste. Meanwhile, a decrease in the total detectable product yield in PC/H_2O was observed at 140°C after 15 min and 150°C after 10 min (Fig. 1f). This indicates the formation of insoluble humins due to polymerization between sugars and furan derivatives during the catalytic conversion of biomass at a higher temperature[11,42].

Comparing paper towel conversion at 130°C, no dehydration product was detected in the H_2O (100%) and DMC/H_2O solvents; conversely, dehydration-rehydration products were detected in the PC/H_2O and EC/H_2O solvents starting from 10 min of reaction time (Fig. 4b). This suggests the higher potential of PC and EC for tandem biomass hydrolysis and dehydration-rehydration reactions. A notable LA yield (~6 Cmol%) generated in PC/H_2O under mild reaction conditions (130°C, 20 min) suggests that PC might be a preferable solvent for LA synthesis from lignocellulosic biomass. The yield of LA could not be determined for EC/H_2O solvent system due to technical issues (LA peak overlapped solvent peak). However, a substantial yield of FA (~6-7 Cmol% at 130°C, 15-20 min) was detected in the EC/H_2O solvent, possibly inferring the yield of LA in the solvent system as LA and FA are coproduced during the catalytic conversion of biomass and sugars[10,43,44].

Energy requirement for sugar production.

Energy requirement for sugar production was estimated and compared for different solvent systems (Reaction conditions: 5 wt.% substrate loading, temperature: 130°C, duration: 10 min, 0.135 M H_2SO_4, solvent ratio: 1:1) based on the power consumption rate recorded in the microwave reactor (Table 3). Energy requirement for ramping (up to 130°C at a ramp rate of 32°C min^{-1}) and reaction (holding at a constant temperature) were estimated separately and then added up to determine the energy consumption per unit of sugar produced in different solvent systems. The results revealed a lower energy requirement (~0.03 kWh) at the ramping stage for carbonate solvent-water binary systems, in contrast, H_2O only required relatively higher energy (~0.05 kWh) for heating up the reaction mixture. Furthermore, binary solvents exhibited a lower energy consumption per unit of sugar production (Table 3) than that of H_2O, as low as 0.002 kWh mol^{-1} in EC/H_2O, which was the most efficient solvent system in terms of energy requirement for sugar production from paper towel waste.

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^{-1})
	Ramp	Reaction	Total		
PC/H_2O	0.034	0.036	0.071	11.19	0.006
EC/H_2O	0.033	0.007	0.040	18.98	0.002
DMC/H_2O	0.037	0.035	0.073	5.91	0.012
H_2O	0.05	0.062	0.110	8.04	0.014

(Reaction conditions: 5 wt% substrate loading, temperature: 130°C, duration: 10 min, 0.135 M H_2SO_4, solvent ratio: 1:1)

Conclusions

The investigated organic carbonate binary solvents, i.e., PC/H_2O and EC/H_2O, effectively facilitated the depolymerization of lignocellulosic paper towel waste under mild reaction conditions. This study explored the potential roles of carbonate solvents in the catalytic system. Higher availability of reactive protons in these solvent systems and autogenous pressure development might favor the breakdown of cellulosic fibers compared to H_2O only. Besides, a considerable amount of sugar derivatives was detected in PC/H_2O and EC/H_2O (at a higher temperature and longer duration), suggesting the suitability of solvents for tandem hydrolysis and dehydration of biomass. The study implies that PC and EC have a high potential to be considered as greener alternatives to commonly used industrial solvents for the efficient valorization of biomass. However, these solvents have a high boiling point (242-248°C), which can be challenging for product separation and solvent recovery by distillation. Future research efforts can be directed to address this issue by selective adsorption for possible implementation of these alternative solvents on an industrial scale.

Note. The authors declare no conflict of interest.

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