Influence of green solvent on levulinic acid production employing lignocellulosic paper waste

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Highlights:

- Green co-solvent systems enhanced depolymerization and LA production
- Maximum 32% of levulinic acid (LA) yielded in GVL/H₂O solvent at 200°C
- GVL/H₂O system maintained high availability of soluble sugars
- Acetone/H₂O solvent generated 17 Cmol% of LA at relatively low temperature (180°C)
- Higher temperature induced polymerization of sugars in Acetone/H₂O solvent

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Abstract

Lignocellulosic wastes constitute a significant portion of the municipal solid waste, which should be valorised for the synthesis of value-added chemicals to achieve circular bioeconomy. This study evaluates the use of γ -valerolactone (GVL) and acetone as green co-solvents to produce levulinic acid (LA) from lignocellulosic paper towel waste, at different temperatures using dilute H₂SO₄. At highest reaction temperature (200°C), water alone as a reaction medium achieved ~15 Cmol% LA at maximum. while A mixture of GVL and water (GVL/H2O) enhanced the depolymerization of paper towel waste and the subsequent conversion to LA, with the highest yield amounted to ~32 Cmol%. Acetone/H2O solvent system generated 17 Cmol% LA at a relatively lower temperature of 180°C, and higher temperature-induced polymerization of soluble sugars and/or intermediates, hindering further conversion to LA. In contrast, the availability of soluble sugars tended to be higher in the GVL/H₂O system, which favoured the production of LA.

Keywords: Waste valorisation; lignocellulosic biomass; sustainable biorefinery; γ-valerolactone;
paper waste.

1. Introduction

Valorisation of lignocellulosic biomass as a renewable feedstock has attracted considerable research interest in producing building-block chemicals in recent years (Yu et al., 2018; Yu et al., 2017b; Chen et al., 2017b). Biomass offers numerous benefits as an alternative to petroleum-derived feedstocks considering its abundance, low cost, renewability, and diversified applications. In addition, utilization of waste biomass (e.g., crop residue, food waste, paper waste) contributes further toward sustainability as it does not necessarily compete with food production yet caters the growing need for biorefineries (Yu et al., 2018; Serrano-Ruiz et al., 2011).

Levulinic acid (LA) represents a promising intermediate for producing valuable chemicals with diversified applications e.g., y-valerolactone (GVL), levulinate esters, succinic acid, diphenolic acid, hydrocarbon fuels, etc. (Dutta et al., 2019; Chen et al., 2017a; Antonetti et al., 2016). LA can be produced from the acid treatment of sugars/monosaccharides or through acid hydrolysis of biomass consisting of cellulose (C₆ sugars) and hemicellulose (C₅ sugars). Production of LA from waste biomass is an important aspect concerning sustainable biorefinery development (Antonetti et al., 2016).

A variety of waste biomass has been explored for the production of LA, for instance, food waste (Chen et al., 2017b; Wang et al., 2015), paper waste (Chen et al., 2018a; Raspolli Galletti et al., 2012), rice husk and straw (Bevilaqua et al., 2013; Yan et al., 2008), etc. generally employing mineral acids such as H₂SO₄ and HCl or solid acid as catalyst (Antonetti et al., 2016). In particular, paper towel waste represents a waste stream that contains a high amount of cellulosic fibres (~70%) and can be easily separated at source (e.g., commercial buildings) (Chen et al., 2018a). According to the US Environmental Protection Agency (EPA), approximately 3.7

million tons of tissue paper and towel (excluding washroom tissue) was generated in 2015,
which requires an efficient recovery and recycling process to divert them from landfill disposal
(US EPA, 2017). Moreover, other treatment (e.g., anaerobic digestion) or recycling techniques
are deemed unsuitable due to low degradability of cellulosic fibres in paper towel and hygiene
concerns. Therefore, developing efficient technology is necessary for paper waste treatment and
valorisation. In this regard, paper towel wastes, which are rich in cellulose, can be potentially
used as the feedstocks for LA production (Chen et al., 2018a; Antonetti et al., 2016).

The solvent is a significant parameter that influences biomass feedstock conversion. In this process, it can interact with reactants or intermediate species and thereby can influence the reaction rate and equilibrium as well as regulate the productivity and selectivity in the system (Yu et al., 2018; Dyson and Jessop, 2016). Appropriate solvents can enhance the valorisation of lignocellulosic waste to produce valuable chemicals. Owing to their crucial contribution to catalysis, it is important to devote research effort for identifying potential solvent for specific catalytic reactions (Dyson and Jessop, 2016).

As an environmentally benign and green solvent, water has been preferred and utilized extensively for biomass fractionation and chemical production by many researchers (Licursi D. et al., 2018; Cao et al., 2018; Raspolli Galletti et al., 2012). Besides, organic solvents (e.g., dimethyl sulfoxide (DMSO), tetrahydrofuran (THF)) and ionic liquids have been employed owing to their influence on the acidic proton, high reactivity of reagents and product selectivity as well as their capability to enhance tandem catalytic reactions for biomass conversion (Yu et al., 2018; Chen et al., 2017a; Chen et al., 2017b; Antonetti et al., 2016). However, these conventional solvents are considered problematic or even hazardous due to safety, health and environmental implications (Prat et al., 2016). Therefore, the selection of an appropriate solvent

is necessary by addressing their 'green' characteristics as well as maintaining reactivity and product selectivity in order to achieve efficient and sustainable LA production. Based on the CHEM21 solvent selection guide (Prat et al., 2016) and previous studies on the effective conversion of biomass to LA, GVL and acetone were selected in this study along with H₂O (the greenest solvent). Their properties are given in Table 1.

GVL is a green solvent in view of its high biodegradability, low toxicity, and very low peroxide formation rate (Horváth, 2008). Moreover, it can be derived from biomass feedstock (Dutta et al., 2019). The use of GVL has been reported for enhancing various biorefinery reactions, e.g., achieving high yield of levulinic acid (Yu et al., 2018; Mellmer et al., 2014a; Alonso et al., 2013a; Wettstein et al., 2012). Acetone is a commonly used and cheap solvent which has been used for effective fractionation of lignocellulose (Smit and Huijgen, 2017; Huijgen et al., 2010) and conversion of biomass to platform chemicals (Chen et al., 2018b; Yu et al., 2017a; Hu et al., 2012). Both GVL and acetone are a polar aprotic solvent that is advantageous for biomassupgrading reactions (Antonetti et al., 2016), (Mellmer et al., 2019). They have polarity (Table 1) comparable to that of the widely used organic solvent DMSO ($\pi^* = 0.94$), and thus may enhance the catalytic conversion of paper towel waste.

This study examines the use of green co-solvents in a binary organic solvent-water (1:1 v/v) system (GVL/H₂O and acetone/H₂O) for conversion of lignocellulosic paper towel waste to LA (as demonstrated by our previous studies, 1:1 ratio of organic solvent-water combination is feasible for conversion of bio-waste (Yu et al., 2018; Chen et al., 2017b)), using dilute sulphuric acid (H₂SO₄) as the catalyst at different temperatures. Interactions between the solvent and substrate will be discussed to elucidate their significance in determining the depolymerisation of lignocellulosic fibre and the formation of LA. The results were verified using standard sugars

(glucose and xylose) as substrates under selected reaction conditions. This study generates insight into the potential roles of green solvents in a catalytic biorefinery in addition to providing a medium. Furthermore, insight obtained for catalytic conversion of paper towel wastes can be helpful for developing a better understanding of the thermochemical conversion of other types of paper wastes that constitute a major portion of municipal solid wastes generated worldwide.

2. Materials and methods

2.1.Paper towel waste and chemicals

Virgin pulp (VPT) and recycled pulp paper towel (RPT) wastes were collected from the Terminal Hall of the Hong Kong International Airport. Paper towel wastes were dried in an oven at 105°C for 48 h and then blended (German Pool, Pro-6) to achieve fibre-like consistency. The composition of lignocellulose is taken as determined by the previous study on paper towel conversion from our group; the characteristics of paper towel waste are presented in Table-2. Sulphuric acid (H₂SO₄, 98%, Honeywell Fluka) was employed as the catalyst for paper towel conversion. The solvents were GVL (98%, J & K Chemicals, China) and acetone (99%, Anaqua, USA). The standard compounds/chemicals for catalytic reaction and calibration of analytical equipment included levulinic acid (98%), formic acid (98%), and cellobiose from Alfa Aesar; glucose (99%, UNI-chem, China); fructose (≥99%) and maltose monohydrate (98%) from WAKO; furfural (99%) and hydroxymethylfurfural (HMF; ≥99%) from Sigma Aldrich; and levoglucosan from Fluorochem. All standard compounds/chemicals were used as received without any alteration.

2.2.Catalytic conversion

The catalytic conversion of paper towel waste was conducted under microwave heating (Ethos Up Microwave Reactor, Milestone, at maximum power of 1.9 KW). For each catalytic run, 10 ml of solvent (100% H₂O or mixture of H₂O and organic solvent (GVL or acetone), 1:1 v/v) was used along with 5 wt/v% substrate loading (paper waste) and 0.135 M H₂SO₄ following method previously reported in studies by our research group (Yu et al., 2018; Chen et al., 2018a). The mixed solvent system is denoted as GVL/H2O and acetone/H2O. The reaction temperature varied from 160 to 200°C for each solvent system and 5 min reaction time was employed for each run after heating the reactor to the required temperature following a constant ramp rate. The reacting vessels were subjected to autogenous pressure with a maximum pressure set as 50 bar for the microwave reactor. After the reaction, vessels were cooled down through mechanical ventilation for 20 to 40 min depending on the reaction temperature. Each catalytic run consisted of two replicates. Conversion of standard sugars (i.e., glucose and xylose) were conducted following same method in different solvent system at 180°C to understand solvent effect on model compounds and to compare with paper towel conversion. Control tests without paper towel were carried out in all solvent system at 200°C.

2.3. Preparation and analysis of liquid samples

After the catalytic run, the liquid samples were obtained from each replicate, diluted with deionised water (DIW) (1:3, v/v) and filtered through a 0.45 μ m pore size membrane filter before analysis. Quantification of products was conducted by high-performance liquid chromatography (HPLC) employing an Aminex HPX-87 column (Bio-Rad) and Chromaster equipment consists of a refractive index detector (Hitachi, Japan). The mobile phase comprises 0.01 M H₂SO₄ at 0.5 ml min⁻¹ flow rate at 50°C column temperature (Yu et al., 2019). Samples spiked with standard

compounds with known concentrations were injected at the beginning of each analytical measurement in order to ensure quality. More information on the analytical procedure can be found in our previous papers (Chen et al., 2018a; Yu et al., 2017b). The yield of products was calculated based on the carbon content of the substrate using the following equation (1) (Yu et al., 2019; Chen et al., 2018a) -

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

137 Where $Conc_p$ denotes the concentration of the products. MW_p and C_p represent the molecular 138 mass and mole number of carbons per mole of the product, respectively. C_s represents the total 139 mole number of carbons in cellulose and hemicellulose fraction of paper towel (0.5 g) as given in 140 Table 2. A volume loss varying from 5-20% (at different temperatures) was recorded for the 141 acetone/H₂O solvent system, which was accounted for the yield calculation. There was no loss of 142 solvent recorded for the H₂O and GVL/H₂O systems.

2.4. Analysis of solid samples

Analysis of post-reaction solid residue as well as untreated paper towel waste was conducted through solid-state 13C NMR and X-ray diffraction (XRD). For selected reaction conditions (all solvent systems at 180°C), solid residues were collected through centrifugation, decantation, washing with DIW, drying, and grinding, afterward subjected to NMR and XRD analysis. Solid-state 13C CP/MAS (cross-polarization/magic angle spinning) NMR was conducted using the JEOL JNM-ECZ500R with the magnetic field strength of 11.6 T at 500 MHz involving 32.7 ms acquisition time, 2 ms contact time, and 5 s relaxation delay. Peak picking of acquired spectra was conducted by using the software MestReNova 14.0.1 for further analysis. XRD analysis was performed by Rigaku Smatlab equipment employing scanning range $2\theta = 10^{\circ}$ to 50° at a rate of

10° min-1 at 45 kV and 200 mA. Crystallinity index (*CrI*) was calculated for samples according
to the method reported in literature (Chen et al., 2018a; Lu et al., 2015).

3. Results and discussion

3.1. Influence of green co-solvent system on depolymerisation of paper towel at different temperatures

The addition of the organic co-solvent to water medium (GVL/H₂O and acetone/H₂O) enhanced the depolymerisation of cellulose and hemicellulose in view of the higher total sugar yields, e.g., \sim 30-36% at 160-170°C compared to \sim 18-22% in H₂O only system (Figure 1). The maximum sugar yield at H₂O only system observed at 190°C (\sim 35 Cmol%) is comparable to the total sugar yield at 170°C in green co-solvent system (\sim 30-36 Cmol%), which suggests that the addition of green co-solvent increased the level of hydrolysis and decrease the energy required for reaction.

Considering high yield of sugars, GVL/H₂O was the most efficient co-solvent for depolymerization of paper towel (~36-40 Cmol% at 170-180°C). Enhanced depolymerisation of paper towel waste in the GVL/H₂O can be attributed to the combined effect of GVL solvent on solvation of cellulose, disrupting cellulose crystallinity and positive influence on glycosidic bond cleavage (Luterbacher et al., 2014; Mellmer et al., 2014a; Mellmer et al., 2014b). It has been reported that GVL can solubilize lignocellulosic biomass and disrupt the structure of crystalline cellulose, leading to increased production of sugars (Luterbacher et al., 2014). Besides, the polar aprotic nature of GVL helps to enhance the reactivity of proton through stabilization of solvated proton compared to reaction condition in H_2O and thereby accelerate the reaction rate for biomass conversion during acid hydrolysis (Mellmer et al., 2014a; Mellmer et al., 2014b).

Moreover, GVL/H_2O solvent has been reported to significantly decrease the activation energy for disaccharide (e.g., cellobiose, maltose) hydrolysis through promoting glycosidic bond (β -1,4 and α -1,4) cleavage, thereby giving a higher reaction rate compared to using 100% H₂O as the solvent; analogous effect is anticipated for cellulose hydrolysis (Mellmer et al., 2014a).

The yield of total soluble products for VPT (Figure 2) reached maximum at 180°C for GVL/H₂O (~51 Cmol%) and acetone/H₂O (~47 Cmol%) which is comparable for green cosolvent systems. The total soluble product yield remained almost same at 180-200°C for GVL/H₂O solvent (~50 Cmol%), while for acetone/H₂O solvent, a considerable drop in the total product yield was observed at higher reaction temperature (~39 Cmol% at 190-200°C). For acetone/H₂O solvent on average, 5-20% of the solvent loss was recorded during the experiment at different temperatures and char formation was observed at 180-200°C. Solvent loss in acetone/H2O system may occur due to self-condensation of acetone or direct condensation of acetone to sugars and sugar derivatives (Smit and Huijgen, 2017), which might be related to lower total sugar yield detected for acetone/H₂O co-solvent system. A previous study (Hu et al., 2012) demonstrated that acetone generated the highest fraction of insoluble polymers among various organic solvent tested (e.g., alcohols, chloroform, DMSO, etc.) for acid-treatment of levoglucosan. In acid-catalysed reactions, acetone can produce different products through intramolecular aldol condensation that ultimately form polymers as well as, condensation products can react with sugars leading to polymer formation (Hu et al., 2012). An isolated phase of products can form through precipitation in the system if the solvent cannot dissolve kinetic products during the reaction (J. Dyson and G. Jessop, 2016). In acetone/H₂O system, polymerisation might have restricted the amount of soluble sugars in reaction medium, and the

solid polymers might have converted to char at higher temperatures, resulting in lower sugar yield in liquid samples in the experiment.

3.2. Effects of green co-solvent on LA production

In general, all solvent systems showed an increasing trend for LA yields from paper towel wastes with increasing temperature, in the presence of dilute H₂SO₄ (0.135M) catalyst, in accordance with the literature (Chen et al., 2017b; Wettstein et al., 2012) (Figure 1). The lower temperature of 160-180°C was efficient for sugar production, and LA emerged at a higher temperature of 180-200°C. At highest reaction temperature (200°C), LA yields of 15-32 Cmol% can be resulted that are comparable to those reported in the previous studies on biomass conversion, such as paper towel waste (LA yield 30-46 Cmol%) (Chen et al., 2018a), paddy straw (LA yield ~24 wt%) (Yan et al., 2008) and paper sludge (LA yield ~15-32 wt%) (Raspolli Galletti et al., 2012).

Although H₂O only solvent alone generated considerable yield of sugars (~60 Cmol% at 180°C) in 0.135 M H₂SO₄ catalyst, its generated only ~2-15% LA yield at 180-200°C (Figure 2), which is similar to values mentioned in previous studies (Chen et al., 2017b; Alonso et al., 2013a). In comparison, GVL/H₂O and acetone/H₂O green co-solvent systems achieved higher LA yields, which were approximately 29-32 Cmol% at maximum, highlighting that the presence of GVL and acetone favoured the tandem dehydration-rehydration reactions.

Comparing the co-solvent systems, acetone/H₂O gave a considerable yield of LA (17 Cmol%) at a relatively lower temperature (180°C), whereas GVL/H2O could not generate significant LA yield until 190°C (~20 Cmol%). For GVL/H2O system, no HMF was detected in solution subjected to reaction at 160-200°C (Figure 2) indicating HMF was readily rehydrated to LA in the solvent system. On the other hand, HMF was available in solution for acetone/H₂O system

except for 200°C treatment, along with higher LA yield at 170-180°C compared to GVL/H₂O, suggesting that dehydration of sugar to HMF was faster in acetone/H₂O compared to GVL/H₂O system. Our previous study (Yu et al., 2017a) showed that acetone/H₂O can provide a faster sugar to HMF conversion rate compared to other organic solvent-water systems like DMSO/H₂O and THF/H₂O. Moreover, faster sugar conversion in acetone/H₂O system can be attributed to the significant pressure build-up in the reaction vessel, which was ~ 30 bar on average (Figure 3) during reaction at 180°C, as the boiling point of acetone is low (56°C). High *in-situ* pressure was reported to accelerate the conversion of biomass/sugars (Yu et al., 2018; Duo et al., 2016). Alternatively, the average in-vessel pressure recorded for GVL/H₂O system was ~12 bar during reaction at 180°C (Figure 3), so, in situ pressure might not have noticeable effect on catalytic conversion in the system.

In case of GVL/H₂O solvent, LA yield was comparatively low at lower temperatures (~2 to 4 Cmol% at 160-180°C). However, with increased temperature (190-200°C), the reactions were accelerated, and a higher yield was achieved (LA yield ~20-32 Cmol%). Despite faster conversion of sugars to LA (17 Cmol%) at 180°C, acetone/H2O system did not provide significant increase in yield (~29 Cmol%) when reaction temperature was further increased to 200°C, whereas GVL/H₂O system generated 8 times higher yield (~32 Cmol%) at 200°C compared to that of at 180°C (~4 Cmol%). The relatively lower yield of LA in acetone/ H_2O can be attributed to the polymerisation

of sugars and condensation products in the solvent system (Hu et al., 2012), which might have restricted the availability of soluble sugars during catalytic reactions at a higher temperature. In contrast, performance of GVL/H_2O solvent system for tandem catalytic reactions can be attributed to the good interactions among substrate, solvent (GVL) and acid catalyst, as GVL has

been reported to solubilize cellulose and products generated during deconstruction of cellulose
(Mellmer et al., 2014a; Alonso et al., 2013a; Wettstein et al., 2012).

To probe the effect of solvent on paper towel conversion, supplementary tests were done with glucose (standard compound) at 180°C in all solvent systems. Using glucose as feedstock, both GVL/H₂O and acetone/H₂O solvent systems produced ~16 Cmol% of LA at 180°C (Figure 4). In comparison, the LA yield from paper towel waste was lower in GVL/H₂O (~4 Cmol%) than that in acetone/H₂O (~17 Cmol%). This results suggest that acetone/H₂O might work more efficiently or faster on depolymerization of lignocellulosic biomass and its subsequent conversion to HMF compared to GVL/H₂O solvent, though polymerization and humin formation at high temperature might restrict the sugars in soluble forms for acetone/H2O, which can ultimately influence LA production.

In general, conversion of RPT was slightly higher than that of VPT in H₂O and acetone/H₂O solvent (Fig.2a and c) which might be related to the relatively shorter fibre length and lower crystallinity of RPT fibres (65.5%) compared to VPT (67.1% crystallinity), as amorphous cellulose and short fibres are easier to be deconstructed (Chen et al., 2018a). In contrast, GVL/H₂O showed slightly lower conversion for recycled pulp at temperatures 160-170°C, and at higher temperatures GVL/H₂O provided almost the same conversion for both types of paper towel waste (Fig.2b). It should be noted that RPT contains more lignin (11.8%) (Table 2) and lignin solubility is high in GVL/H₂O solution where GVL concentration ranges between 50-65 wt% (Lê et al., 2016), and reactions may slow down due to high solute-solvent solvent interactions (Dyson 2016) GVL. and Jessop, between lignin and Results from paper towel conversion revealed that hemicellulose conversion remained facile in all solvent systems for both VPT and RPT (Figure 2), as efficient production of xylose was

recognised which was consequently dehydrated to furfural. Furfural production occurred to a higher extent at a lower temperature (160°C) than that of LA indicating that deconstruction of hemicellulose and subsequent conversion to furfural were less energy-intensive compared to cellulose. At 190-200°C a higher yield of furfural was observed for GVL/H₂O (~9-11 Cmol%) while a lower furfural yield was observed for acetone/H₂O (~3-4 Cmol%). It is worth mentioning that, GVL can decrease the rate of furfural degradation (Alonso et al., 2013b), which is reflected in the results of this study. In contrast, acetone may react with furfural and form condensation product (Hu et al., 2012). Our supplementary test with xylose (standard compound) (Figure 4) revealed that only ~50 Cmol% of the total products were detected in solution and considerable amount of black solids was observed in acetone/H₂O system.

3.3. Analysis of solid residues subjected to the reaction in different solvents

As observed during the experiment, a high amount of solid residue was generated after reaction in 100% H₂O which can be related to the lower depolymerization and low LA yield in water as a large fraction of lignocellulosic fibre might remain unreacted or generated humins. As solid residue was collected and measured for reactions at 180°C, it was observed that reaction in GVL/H₂O solvent generated 50% less solid residue compared to H₂O only system. On the other hand, for acetone/H₂O system formation of char was observed at the bottom of the reaction vessel and exact fraction of solids was not possible to quantify. Less quantity of unreacted solids in GVL/H₂O solvent system indicates higher solubility and conversion of paper towel waste during reaction.

To understand the changes in paper towel wastes subject to the reaction in different solvent systems, solid-state ¹³C NMR (CP/MAS) was obtained for remaining solids after reaction and paper towel waste before reaction. NMR spectra of paper towel wastes and post-reaction solid

> residue (Figure 5) resemble the resonances observed in the spectrum of isolated cellulose which can be related to the high cellulosic fractions in paper towel waste (78.1% in VPT waste). According to literature, chemical shifts given by a ¹³C CP/MAS NMR spectrum of cellulose ranges from 100-108, 80-93, 70-80 and 57-70 ppm can be respectively assigned to C1, C4, C2.3.5 and C₆ signals of cellulose (Alcántara et al., 2016; Foston, 2014; Kim et al., 2013; Kono et al., 2002; Atalla and VanderHart, 1999). Considering the peak attribution given above and diversity of cellulosic biomass, NMR peaks obtained from unreacted solid samples might be assigned as follows: the peak at 101 ppm is assigned to C₁, peaks at 79 and 85 are assigned to C₄, peaks at 71 and 68 are assigned to $C_{2,3,5}$ and peaks at 61 and 58 are assigned to C_6 signals of cellulose respectively.

> The C₄ peak of NMR spectra is commonly utilized by researchers to extract structural information of cellulose. A broad peak range from 80-85 ppm represents C₄ cellulose amorphous carbon, whereas a comparatively sharper peak from 85-92 ppm represents C₄ crystalline carbon (Zhu et al., 2016; Foston, 2014; Cao et al., 2012). The C₄ peaks (85 and 79 ppm) of the 13 C NMR spectrum of paper towel waste before reaction (Figure 5) shows that the intensity of amorphous carbon is relatively higher compared to that of crystalline carbon. In contrast, spectra of solid residue after reaction in different solvents show alteration in relative intensities of amorphous and crystalline carbon. Following acid treatment in different solvents, the intensity of crystalline carbon increased while the intensity of amorphous carbon decreased compared to that of untreated paper towel waste (Figure 5). This shift might indicate that amorphous carbon has been consumed during reaction to produce sugar and relative crystallinity has increased thereby crystalline phase gave relatively higher resonance (Zhu et al., 2016; Samuel et al., 2010). An increase in crystallinity is usually reported after acid hydrolysis of biomass as amorphous carbon

is more susceptible to degradation (Chen et al., 2018a; Bernardinelli et al., 2015). The change in relative intensities of crystalline and amorphous carbon (Figure 5) is less pronounced in the solid residue obtained from a reaction involving H₂O only solvent system, however, it is more pronounced in green co-solvent system involving GVL/H₂O and acetone/H₂O. Similar changes in relative intensities of crystalline and amorphous phase can be also observed for the C6 peak of spectra (Samuel et al., 2010). This phenomenon might indicate that higher amount of amorphous carbon was converted during reaction in GVL/H₂O and acetone/H₂O solvent system compared to 100% H₂O, which is in good agreement with the total yield of soluble products that is 38 Cmol% for H₂O only solvent system and ~50 Cmol% for GVL/H₂O and acetone/H₂O co-solvent system.

The XRD spectra of solid residue subjected to reactions in different solvent systems (Figure S1) have been analyzed to reveal the changes in cellulose crystallinity. The diffraction peaks were identified at 15°, 22.5° and 34.5° corresponding to (110), (200) and (004) planes of Type-I crystalline cellulose (Chen et al., 2018a; Lu et al., 2015). The calculated CrI values (Table 3) demonstrated the changes in crystallinity after reaction compared to untreated paper towel waste yet significant alteration in cellulose crystallinity was not observed. Evaluating CrI values for solid samples subjected to reactions in different solvent systems showed a relatively higher crystallinity for GVL/H₂O and acetone/H₂O compared to H₂O only system. This might suggest a higher degree of hydrolysis of amorphous cellulose in co-solvent systems that leaves behind the crystalline form in cellulose structure, thus relative crystallinity may increase in solids (Chen et al., 2018a).

Comparing organic solvent-water binary solvent systems, GVL/H₂O and acetone/H₂O provides
 advantages from different viewpoints. To achieve a higher LA yield from lignocellulose at lower

temperature acetone/H2O can be efficient where GVL/H2O provides a slower conversion of sugars. To maintain availability of soluble sugars and further enhancement of LA yield GVL/H₂O system is beneficial. However, green co-solvent systems can be tuned for optimum LA production considering reaction temperature, duration and acid concentration, as well as experiments, can be performed to reveal conversion kinetics for the co-solvent system to optimize the process. On the other hand, to obtain a sustainable biomass conversion process, recovery of solvent is important; in that case acetone/H2O system falls short owing to considerable solvent loss during reaction. Moreover, working with acetone at high temperatures raises safety concerns as its flashpoint is very low -18 degree (Prat et al., 2016) which can be an issue concerning its significance as a green solvent. Hence, careful attention should be given for selecting green co-solvent system for biomass to chemical conversion considering reaction conditions, product selectivity, environmental impact and safe handling of chemicals at work.

4. Conclusions

This study investigated the effect of organic solvent-water binary green solvent systems on the acid hydrolysis of lignocellulosic paper towel waste to produce LA. Depolymerization of fibres and yield of LA was enhanced by green co-solvents compared to 100% aqueous condition. Acetone/H₂O gave a considerable yield of LA at a relatively lower temperature (180°C), whereas GVL/H₂O maintained the availability of sugar through solubilization of by-products and further enhanced the yield of LA. This research implies that green solvents like GVL and acetone have good potential for catalytic conversion of high cellulose-containing wastes like paper wastes.

Conflict of interest

356 There is no conflict of interest to declare.

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363 Appendix A. Supplementary data

364 Supplementary data associated with this article can be found (to be confirmed)

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Influence of green solvent on levulinic acid production employing lignocellulosic paper waste

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Figure 1. The yield of total sugars (cellobiose, glucose, levoglucosan, and xylose) and LA at different temperatures (160-200°C) in H₂O, GVL/H₂O, and acetone/H₂O solvent system (VPT only) (reaction conditions: 5wt% substrate, 0.135M H₂SO₄, 5min, solvent mixture 1:1)



Figure 2. Product yields from paper towel conversion in (a) H₂O, (b) GVL/H₂O and (c) acetone/H₂O solvent system at different temperature utilizing VPT and RPT (reaction conditions: 5wt% substrate, 0.135M H₂SO₄, 5min, solvent mixture 1:1)



Figure 3. Temperature and pressure profile during the reaction (paper towel conversion) in (a) GVL/H₂O and (b) acetone/H₂O system (reaction conditions: 5wt% substrate, 0.135M H_2SO_4 , 5min, 180°C, solvent mixture 1:1)



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Table 3:Crystallinity index (CrI) of VPT subjected to reaction in different solvents
(reaction conditions: 5wt% substrate, 0.135M H2SO4, 5min, 180°C, solvent
mixture 1:1)

Solvent	Polarity (π^*)	Boiling point (°C)	Flashpoint (°C)
H ₂ O	10.09	100	na
GVL	0.83	207	100
Acetone	0.71	56	-18

Table 1: Properties of selected solvents (J. Dyson and G. Jessop, 2016; Prat et al., 2016)

Table 2: Characteristics of the paper towel waste used for catalytic conversion (Chen et al., 2018a)

Туре	Cellulose	Hemicellulose	Lignin	Crystallinity index (CrI)
VPT	78.1% (13.03)*	20.6% (3.44)*	1.3%	67.1
RPT	67.4% (11.23)*	20.8% (3.45)*	11.8%	65.5

* Number in the parentheses represents the mole number of carbon for 0.5 g of corresponding paper towel waste;

VPT and RPT were manufactured from raw materials/sources (Chen et al., 2018a).

Table 3: Crystallinity index (*Crl*) of VPT subjected to reaction in different solvents (reaction conditions: 5wt% substrate, 0.135M H₂SO₄, 5min, 180°C, solvent mixture 1:1)

Reaction conditions	CrI (%)
Untreated paper towel waste	67.1 (Chen et al., 2018a)
H ₂ O	46.9
GVL/H ₂ O	50.5
acetone/H ₂ O	49.1