Recycled Biorefinery System Integrating Phosphoric Acid/Acetone Pretreatment of Sugarcane Bagasse with Subsequent Platform Chemicals Generation

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In order to minimize the waste of polysaccharides (hemicellulose and cellulose) during preparation of platform chemicals (furfural and levulinic acid) from lignocellulose in one-pot acid/organic solvent systems, a novel two-step biorefinery system was developed based on sugarcane bagasse fractionation with a phosphoric acid/acetone pretreatment method. The effect of different pretreatment conditions on sugarcane bagasse fractionation was studied at first. Under the optimal condition (5 g bagasse, 40 mL 85% phosphoric acid, 50 °C, 1 h, precooled acetone), 72.5% xylose and 74.5% glucose (the residual biomass from pretreatment) were obtained. Acetone was evaporated and removed from the acetone extract, and then the soluble lignin was precipitated and recovered through the addition of water in the extract. The water solution (containing phosphoric acid and 20.8% xylose) and washing water from residue (containing 41.7%% xylose) was combined to produce furfural at 180 °C. Meanwhile, the potential of LA generation from cellulosic residue was evaluated *via* glucose conversion in different phosphoric acid/acetone systems.

Keywords: Furfural; Levulinic acid; Acetone; Phosphoric acid; Sugarcane bagasse; Pretreatment

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INTRODUCTION

Biomass recalcitrance is the natural resistance of plant cell walls to microbial and enzymatic deconstruction (Himmel *et al.* 2007). The cell walls have complicated and compact structures that can be divided into multiple layers, normally including the middle lamella (ML), primary wall (P), and secondary wall (S). The content, distribution, as well as the connection types of cellulose, hemicellulose, and lignin in each layer are different (Yu *et al.* 2013; Zhuang *et al.* 2015). Therefore, pretreatment is a prerequisite to overcome biomass recalcitrance and enhance the biochemical conversion ratio of polysaccharides (Zhang *et al.* 2016).

Organic solvent pretreatment for lignocellulose is an important and efficient technology for the biorefining of lignocellulose. It can dissolve lignin and hemicellulose, leaving cellulosic residue; moreover, lignin can be recovered as a solid material (Zhao *et al.* 2009, 2017). Organic solvent pretreatments with added acids are commonly used because they raise the delignification rate, and a higher xylose yield can be achieved when acid catalysts are added (Zhao *et al.* 2009).

Currently, acid/organic solvent systems are not only suitable for pretreatment, but also for the efficient preparation of high value-added platform compounds, including furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA). Organic solvents that are immiscible with water could form a biphasic system. The immiscible phase extracts the target platform products from the aqueous phase, preventing further reactions in the acid solution and thus enriching and reclaiming the products (Román-Leshkov *et al*. 2006; Burket and Sabesan 2012; Dumesic *et al*. 2012; Gürbüz *et al*. 2012; Shi *et al*. 2013; Yang *et al*. 2013; Zhang *et al*. 2013; Wang *et al*. 2017). Organic solvents miscible with water could form a homogeneous system and change the nature of the reaction system (Román-Leshkov *et al*. 2006). Due to their excellent solvent effect, many organic solvents were tested and adopted to enhance the yields of target platform chemicals (Shuai and Luterbacher 2016; Wang *et al.* 2018).

A one-pot acid/organic solvent system that can produce furfural and HMF, or furfural and LA at the same time is a popular research area (Alonso *et al.* 2013; Cai *et al.* 2013, 2014). However, due to the different characteristics of hemicellulose and cellulose (Wyman *et al.* 2005), and the easily degradable nature of furfural in an acidic environment (Lange *et al.* 2012; Cai *et al.* 2013), high yields of all products were hard to achieve and this wastes hemicellulose or cellulose. Thus, it was suggested that furfural (hemicellulose dehydrated chemical) and HMF (or LA, cellulose dehydrated chemical) should be prepared in separate procedures (Zhao *et al.* 2009; Cai *et al.* 2013; Zhao *et al.* 2017).

If lignocellulose is fractionated by an acid/organic solvent system, and hemicellulose and cellulose are converted to high value-added platform compounds by the same system, the pretreatment's advantages can be used; meanwhile the shortcomings of the system can be avoided. Tang *et al.* (2017) pointed out that the low eutectic solvent (DES) system can be used to fractionate biomass; meanwhile, high yield production of HMF from C6 sugars can be achieved in DES. Unfortunately, the strong interaction between HMF and DES components such as ChCl makes it difficult to separate and purify HMF (Tang *et al.* 2017). There has been a lack of published research about the acids and organic solvents used in the fractionation stage are also used in the following stage of platform compound production.

The phosphoric acid (H_3PO_4)/acetone pretreatment method has been previously investigated by researchers for ethanol production (Zhang *et al.* 2006, 2007; Sathitsuksanoh *et al.* 2009; Rollin *et al.* 2011). Phosphoric acid pretreatment can reduce the crystallinity of cellulose and avoid its further degradation into water-soluble sugar, while avoiding the damage of containers caused by corrosive acids such as sulfuric acid (Zhang *et al.* 2006). By this pretreatment, lignin is soluble in the acetone extract, and high purity of amorphous cellulosic residue is obtained and separated from hemicellulose, which significantly promotes enzymatic hydrolysis and ethanol yields.

In this paper, a phosphoric acid/acetone system was adopted for pretreatment of bagasse to fractionate lignocellulose into water-soluble C5 sugars, acetone-soluble lignin, and solid cellulose residue. Then, preparation of furfural and LA from C5/C6 sugars, catalyzed by phosphoric acid that had been used during pretreatment, was implemented using separate steps. High furfural and LA yields were easily obtained. Using the same catalytic system for pretreatment and its subsequent production of high value-added platform chemicals avoids reagent waste, lowers energy consumption, and reduces cost.

EXPERIMENTAL

Materials

Phosphoric acid (85 wt%, AR) and microcrystalline cellulose were purchased from Fuyu Fine Chemical Co., Ltd (Tianjin, China). Acetone (AR) and glucose (AR) were purchased from Damao Fine Chemical Co., Ltd (Tianjin, China). D-xylose () was purchased from Yuanju Fine Chemical Co., Ltd (Shanghai, China). Furfural (GR) and HMF (GR) were purchased from Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). LA was purchased from Sigma-Aldrich Shanghai Co., Ltd (Shanghai, China). Commercial cellulase (151 FPU/g) was purchased from Imperial Jade Biotechnology Co., Ltd. (Ningxia, China). Bagasse, a very common crop in South China, collected from Guangxi Province (Pingxiang, China) was used as the lignocellulosic feedstock, which was machine milled and screened to 40- to 60-mesh. The particles were oven-dried at 45 °C to a constant mass.

Bagasse pretreatment- Bagasse digestion at different phosphoric acid concentrations

Five grams bagasse and a certain concentration of phosphoric acid solution (liquid/solid ratio =8:1, v:w) were first placed in a pear-shaped bottle. The contents were stirred by a mixing motor at 90 r/min for 1h in a 50 °C water bath (HH-S8, Jiangsu Jinyi Instrument Technology Co., Ltd., Changzhou, China). The reaction condition was similar to the previous report (Zhang *et al.* 2006, 2007). The concentrations of phosphoric acid solutions were 40.0 wt%, 62.5 wt%, and 85.0 wt%. Bagasse was then transferred to a 250-mL Buchner funnel using qualitative filter paper and washed to neutral PH with deionized (DI) water. The solid residue and washing water were separated by vacuum filtration at room temperature. Through the analysis of xylose yields in washing water and glucose yield in solid residue, an optimal phosphoric acid concentration was determined.

Bagasse pretreatment at different conditions

Stirring and reaction equipment also affect the experimental results. This study also investigated the effects of different reaction equipment, stirring conditions, and temperature of acetone added in the subsequent procedure on the pretreatment results. In condition I, bagasse was pretreated by phosphoric acid in a 50-mL pear bottle in a 50 °C water bath, and the digestion was stirred by mechanical stirring for 1 h. Then, precooled acetone (-18 °C) was added into the bottle (m:v = 1:20) as shown in Table 1.

Table 1. Bagasse Pretreatment under Different Types of Conditions

Condition	Equipment	Stirring	Acetone Temperature
I	Pear bottle, water bath	Mechanical stirring	-18 °C
II	Pear bottle, water bath	Mechanical stirring	Room temperature
III	Pear bottle, water bath	None	Room temperature
IV	Pear bottle, rotary evaporator	Rotation	Room temperature

In condition II, the procedures were similar to I, except for the acetone being used at room temperature. In condition III, the procedures were similar to II, except no stirring

was adopted. In condition IV, bagasse and phosphoric acid were added to a 50-mL pear bottle, and then the bottle was equipped in a rotary evaporator (Yuhua Instrument Co., Ltd., Gongyi, China). The stirring was approached by rotation at 90 rpm, and the vacuum part was closed. Lastly, acetone at room temperature was added into the bottles (m:v = 1:20).

Enzymatic hydrolysis

After being separated with acetone supernatants, the residues from condition I, II, III, and IV were washed using DI water until neutral. The washing water and the residue were then separated by vacuum filtration. In order to preserve the moisture property of the residues and reuse the phosphoric acid, the residues were not dried in ovens and added phosphoric acid solution for the following enzymatic hydrolysis (Shi, *et al.* 2014). The moisture contents of the residues were measured. Based on the known moisture content, diluted phosphoric acid solution was added to the residue, to adjust the pH to 4.8; meanwhile the solid/liquid ratio was 20:1 (v:m). Cellulase was added at 30 FPU/g of substrate. Then, enzymatic hydrolysis tests were performed in 100-mL Erlenmeyer flasks for 72 h in a 50 °C thermostat shaker (150 r/min, Chenghui Instrument Plant, Jintan, China).

Acetone-soluble lignin recovery

After pretreatment under optimal conditions, the acetone extract and the residue were separated by vacuum filtration at room temperature. Then, the acetone extract was placed in a vacuum rotary evaporator and evacuated at 60 °C under vacuum environment for 10 min. A total of 75 mL of DI water was added into the remaining concentrated brown liquid to precipitate lignin. The lignin was separated and recovered by centrifugation at 4000 rpm at room temperature.

Preparation of furfural and LA

The preparation of platform compounds was approached using customized 15-mL tubular reactors (1.27 cm in diameter and 15 cm in length, 316-L stainless steel, Fig. 1), which were heated by two homemade sand baths (bath 1 and bath 2). The reactant was loaded into the tubular reactor and sealed with threaded caps. Each cap was equipped with a thermocouple (not shown in Fig. 1). The thermocouple connected with the temperature controller was inserted in the top of the cap, and when the reactant was added, the thermocouple will be immersed in liquid. Before reaction, the temperature of bath 1 was set at 350 °C, and the temperature of bath 2 was set at 180 °C. Both sand baths were preheated for 1 h to keep their temperatures stable at the set values. The sealed tubular reactor was placed in bath 1, with only the cap outside the sand. After a rapid preheating (approximately 1 to 2 min) to reach the reaction temperature, the reactor was quickly transferred to bath 2. The temperature of each reactor was monitored through the digital display on the temperature controller. At different sampling times, the reactors were removed from bath 2 and rapidly immersed in an ice bath for cooling.

For furfural preparation, the pretreated residue was washed with 250 mL DI water. Then, the washing water was mixed with the water solution from the "Acetone-soluble lignin recovery" section at the ratio of 1:1 (v:v). Each tubular reactor was loaded with 10 mL of the mixture and reacted at 180 °C for 0, 15, 30, 45, and 60 min.

For LA preparation, glucose was used as model compound. Four water solutions containing 1 wt% H_3PO_4, 1 wt% H_3PO_4 with 0.5 wt% acetone, 10 wt% H_3PO_4, and 10 wt% H_3PO_4 with 5 wt% acetone, were first prepared. Next, glucose was added into these

solutions with the sugar concentration 20 g/L. Then, each tubular reactor was loaded with 10 mL of solution and reacted at 180 °C for 10, 30, 60, 90, and 120 min.

(a)

(b)

Fig. 1. (a) 15-mL tubular reactors and (b) the sand baths and the temperature controller

Methods

The compositional analysis of raw materials and residues was conducted according to the standard analytical method LAP-002 to evaluate the carbohydrates in bagasse and LAP-003 to evaluate the acid-insoluble lignin (Sluiter *et al*. 2012). In certain situations, secondary hydrolysis with 4 wt% sulfuric acid was required to hydrolyze the xylo-oligosaccharides into monosaccharides. The results of these analyses revealed that lignocellulose was composed of 38.8% glucan (43.1% glucose), 21.3% xylan (23.7% xylose), and 23.8% Klason lignin, all expressed on a dry weight basis.

The surface morphology and characteristics of the raw material and pretreated residues were characterized by scanning electron microscopy (SEM; Hitachi-S4800, Hitachi, Tokyo, Japan). Imaging was performed at a beam accelerating voltage of 2.5 kV, and images were obtained at magnifications of 500× to 5000×.

The specific surface area and the internal pore distribution of solid materials were analyzed by the Brunauer-Emmett-Teller (BET) method and an aperture Analyzer (SI-MP-10/PoreMaster 33, Quantachrome Instruments, Boynton Beach, FL, USA). X-ray diffraction (XRD) of the raw material and residues was performed using an X'Pert Pro MPD (PW3040/60, Philips, Amsterdam, Netherlands) operating at 40 kV and 40 mA by Cu radiation source in the 2θ range from 5° to 100° with a scanning step length of 4°/min.

The monosaccharides, aldehydes, and levulinic acid were detected and quantified using high performance liquid chromatography (HPLC; Model 2695, Waters Corp., Milford, MA, USA) equipped with a Shodex sugar SH-1011 column coupled with a refractive index detector (Model 2414, Waters Corp., Milford, MA, USA) and a photodiode array detector (Model 2998, Waters Corp., Milford, MA, USA). The mobile phase employed with the column was 0.005 M H_2SO_4; a flow rate of 0.5 mL/min and a column temperature of 50 °C were used. Because the peak area of phosphoric acid overlapped the peaks of cellobiose, glucose, and xylose, the concentrations of these sugars had to be determined after neutralization; the concentration of the aldehydes and LA were analyzed

without neutralization. Before injecting the samples into the HPLC, the samples were diluted, centrifuged at 5000 rpm for 5 min, and filtered through a 0.22-μm filter membrane.

Equations

Based on XRD analysis, the crystallinity indices of the raw material and pretreated residue were calculated according to the following equation, where CrI is the crystallinity index, $I_{crystalline(002)}$ is the strength of the crystalline zone (2θ = 22.5°), and $I_{amorphous}$ is the strength of the amorphous region (2θ = 18°).

$$CrI\ (\%) = (I_{crystalline(002)} - I_{amorphous}) / I_{crystalline(002)} \quad (1)$$

The yields of xylose, glucose, furfural, HMF, FA, and LA (Y_x, Y_g, Y_f, Y_h, Y_{fa} and Y_l) were calculated as follows:

$$Y_x\ (\%) = (mass\ of\ xylose) / (mass\ of\ xylose\ in\ bagasse) \times 100 \quad (2)$$

$$Y_g\ (\%) = (mass\ of\ glucose) / (mass\ of\ glucose\ in\ bagasse) \times 100 \quad (3)$$

$$Y_f\ (\%) = (moles\ of\ furfural\ produced) / (moles\ of\ xylose\ reacted) \times 100 \quad (4)$$

$$Y_h\ (\%) = (moles\ of\ HMF\ produced) / (moles\ of\ glucose\ reacted) \times 100 \quad (5)$$

$$Y_{fa}\ (\%) = (moles\ of\ FA\ produced) / (moles\ of\ glucose\ reacted) \times 100 \quad (6)$$

$$Y_l\ (\%) = (moles\ of\ LA\ produced) / (moles\ of\ glucose\ reacted) \times 100 \quad (7)$$

RESULTS AND DISCUSSION

Bagasse Digestion Under Different Phosphoric Acid Concentrations

The acid concentration is the most important factor affecting the acidic pretreatment results, thus a series of bagasse digestion experiments under different concentrations of phosphoric acid were approached. The compositions of the raw material and residues are shown in Table 2. It was found that the xylan and lignin contents in the residues decreased while the glucan contents increased when the concentrations of phosphoric acid increased from 40.0 wt% to 85.0 wt%. This result indicated that the ability of phosphoric acid to remove hemicellulose and lignin and extract cellulosic residue was strengthened when the phosphoric acid concentrations increased.

Figure 2 shows SEM images of the microstructure of raw bagasse and residues following pretreatment with different phosphoric acid concentrations. The raw bagasse particle surface indicated it was composed of many closely arranged thin, long stripes (Fig. 1a). If bagasse was pretreated with 40.0 wt% phosphoric acid, the microstructure of the solid was changed by the destruction of the closely arranged stripes to reveal the vascular network underneath (Fig. 1b). Though the outer surface became rough, there were still regularly arranged fibrous structures. The particle surface of 62.5 wt% phosphoric acid-treated bagasse showed further destruction. Not only was almost the entire vascular network underneath exposed, but also plenty of fiber bundles were fragmented. However, the arrangement of stripes still followed a certain rule (Fig. 1c).

Table 2. Influence of Phosphoric Acid Concentrations on Compositions of Bagasse and Residues

	Glucan (%)	Xylan (%)	Lignin (%)
Bagasse	38.8	21.3	23.8
Residue-40.0 wt% H_3PO_4	39.3	19.7	22.7
Residue-62.5 wt% H_3PO_4	48.6	12.7	20.3
Residue-85.0 wt% H_3PO_4	50.3	5.1	18.9

After 85.0 wt% phosphoric acid pretreatment, the bundle structure of cellulose fibers completely disappeared, and no specific structure remained (Fig. 1d). These changes indicated that the surface destruction of bagasse became severe with increased phosphoric acid concentration. In addition, the crystalline structure of cellulose gradually disappeared as the phosphoric acid concentration increased, which increased the reactivity of acidic hydrolysis or enzymatic hydrolysis.

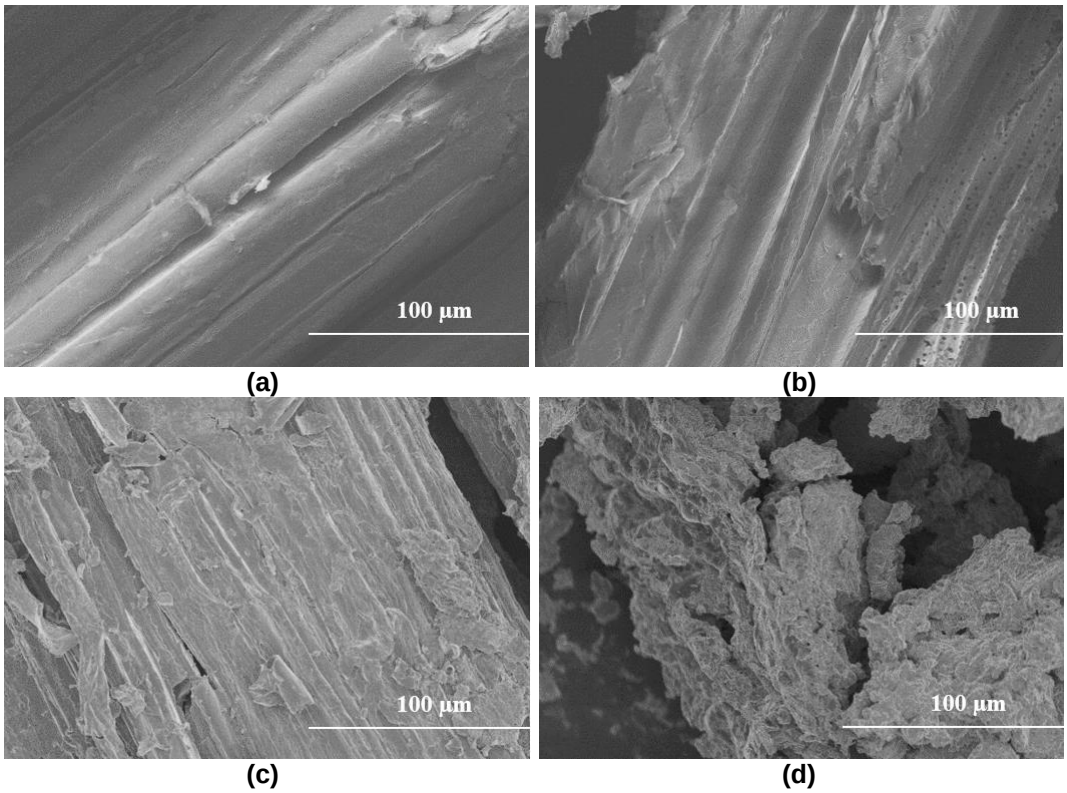

Fig. 2. SEM images of solids at 500× magnification from (a) raw bagasse, (b) 40.0 wt% phosphoric acid-pretreated bagasse, (C) 62.5 wt% phosphoric acid-pretreated bagasse, and (d) 85.0 wt% phosphoric acid-pretreated bagasse; phosphoric acid pretreatment condition: 50 °C, 1 h, acid:solid ratio = 8:1 (v:w)

To further investigate the inner structural changes of bagasse before and after phosphoric acid digestion, the specific surface area, pore volume, and pore radius of bagasse and residues were measured, as shown in Table 3. These specific surface areas reflect the

chance of contact between cellulase and substrate, and are tightly related with the hydrolysis rate and hydrolysis degree of cellulose (Wiman *et al.* 2012). Compared to the raw material, the specific surface area, pore volume, and pore radius of 40.0 wt% phosphoric acid-pretreated residue increased 44.1%, 170.7%, and 162.8%, respectively. The three parameters of 62.5 wt% phosphoric acid-pretreated residue increased 58.6%, 319.2%, 162.8%, respectively, compared to the raw material. The specific surface area of the 85.0 wt% phosphoric acid pretreatment residue slightly increased, but the pore volume and average pore radius decreased 2.4% and 13.2%, respectively, compared to the raw material, which was consistent with the SEM results of the residue.

Table 3. Specific Surface Area, Pore Volume, and Pore Radius of Bagasse and Residues under Different Phosphoric Acid Concentrations

Sample	Specific Surface Area (m^2/g)	Pore Volume (10^{-3}mL/g)	Average Pore Radius (nm)
Bagasse	1.52	4.58	12.10
Residue-40.0 wt% H_3PO_4	2.19	12.40	22.50
Residue-62.5 wt% H_3PO_4	2.41	19.20	31.80
Residue-85.0 wt% H_3PO_4	1.72	4.47	10.50

The cellulose crystallinity is an important factor affecting enzymatic hydrolysis. Therefore, the crystallinities of the raw material and residues from phosphoric acid pretreatment under different concentrations were determined by XRD. In Fig. 3, two obvious peaks are the characteristic diffraction peaks of cellulose, where the peak at 22° represents the maximum diffraction of the important crystal plane (002) of cellulose and the peaks at 18° are the scattering intensity of the non-crystalline background diffraction. It was found that the intensity of peak at 22° decreased sharply with the increase of phosphoric acid concentrations, which indicated the amorphous state of the residue from 85.0 wt% phosphoric acid pretreatment. Also, the amorphous cellulose obtained from 85.0% phosphoric acid pretreatment (nearly total removal of the crystalline structure of cellulose) might be the reason for the pore volume and pore radius decrease in 85 wt%.

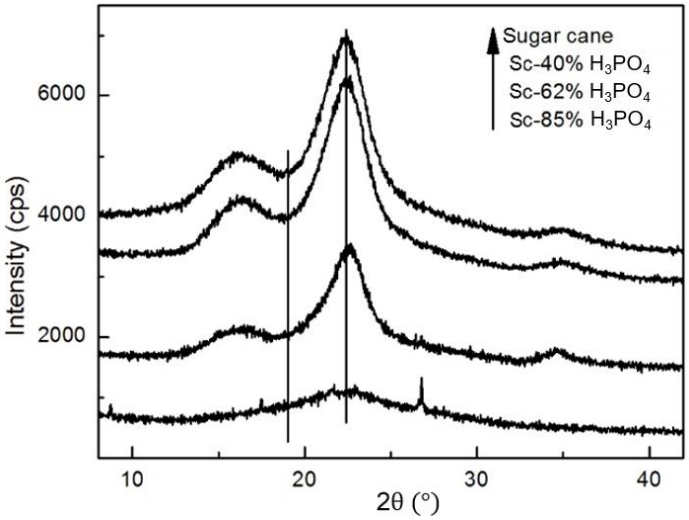

Fig. 3. XRD spectrum of bagasse and pretreated residues under different phosphoric acid concentrations

From Table 4, it was found that the CrI of raw material was 51%, and the CrI of residue-40.0 wt% phosphoric acid was slightly increased. However, the CrI of the other two residues decreased, 49% (residue-62.5 wt% phosphoric acid) and 23% (residue-85.0 wt% phosphoric acid). The results were in accordance with the structural changes of bagasse and residues, as evidenced in Fig. 2.

Table 4. CrI of Raw Bagasse and Pretreated Residues Under Different Acid Concentrations

	$I_{(002)}$	$I_{(amorphous)}$	CrI (%)
Bagasse	4485	2201	51
Residue-40.0 wt% H_3PO_4	4277	1973	53
Residue-62.5 wt% H_3PO_4	4028	1794	49
Residue-85.0 wt% H_3PO_4	1966	1518	23

The above results showed that the changes of the digested residues were remarkably influenced by phosphoric acid concentrations. The residue from the 85.0 wt% phosphoric acid pretreatment exhibited the most obvious change, maximum xylan removal, severely damaged material surface structure, decreased pore volume and average pore size, and a CrI of only 45% of the raw material. The severely damaged cellulosic structure and highest cellulose content of residue from 85.0 wt% acid pretreatment indicated that it can be easily and fully utilized subsequently.

Results of Bagasse Pretreatment Under Different Conditions

Bagasse was pretreated at the fixed 85 wt% acid concentration and under conditions I, II, III, and IV (Table 1). After removing the acetone supernatant and washing, enzymatic hydrolysis of the four pretreated residues was approached for 72 h. The glucose and xylose yields in enzymatic hydrolysates, the xylose yields in washing water of pretreated residues (treated by 4 wt% H_2SO_4), and the total glucose and xylose yields are shown in Table 5. It was found that the total xylose yield from pretreatment in the rotary evaporator (IV) was 84.49% of that from the pretreatment in water bath (II). When pretreatment was carried out *via* water bath, the total xylose yield from non-stirring (III) was 62.7% of that from stirring (II). After phosphoric acid pretreatment in the stirring water bath, pre-cooled acetone (-18 °C) and acetone at room temperature were added to the residues. Furthermore, the total xylose yield from adding acetone at room temperature (II) was 88.6% of that from adding pre-cooled acetone (I). In the water bath experiment, the effect of precooled acetone on the glucose yield in the enzymatic hydrolysate was not obvious. However, precooled acetone could promote the yield of total xylose, which was achieved by slight stimulating the xylose yield in the enzymatic hydrolysate and significant improving the xylose yield in the washing water. Therefore, the optimal pretreatment condition (I) was 85 wt% phosphoric acid digestion in 50 °C stirring water bath for 1 h followed by the addition of precooled acetone (-18 °C).

After pretreatment under condition I, the lignin in the acetone supernatant was recovered as a jelly-like state (Fig. 4). After recovering the precipitated lignin, the upper aqueous solution was analyzed by HPLC, and 0.25 g of xylose was detected.

Table 5. Xylose and Glucose Yields in Enzymatic Hydrolysates and Washing Waters and the Total Sugar Yields Under Different Pretreatment Conditions

	Enzymatic Hydrolysate		Xylose Yield in Washing Water (Treated by 4 wt% H_2SO_4) (%)	Total Glucose Yield (%)	Total Xylose Yield (%)
	Glucose yield (%)	Xylose yield (%)			
I	74.50	10.15	46.08	74.50	56.23
II	72.32	8.27	41.58	72.32	49.85
III	76.24	9.10	22.17	76.24	31.27
IV	13.74	6.54	35.58	13.74	42.12

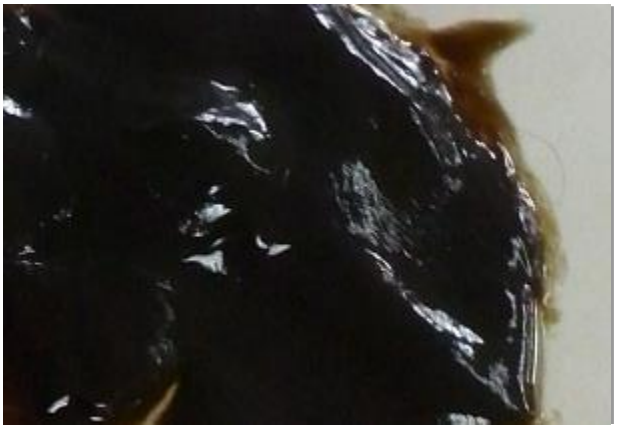

Fig. 4. Recovered bagasse-derived lignin from acetone supernatant under pretreatment condition

The sugar mass balance of pretreated 5 g of bagasse under condition I is shown in Fig. 5.

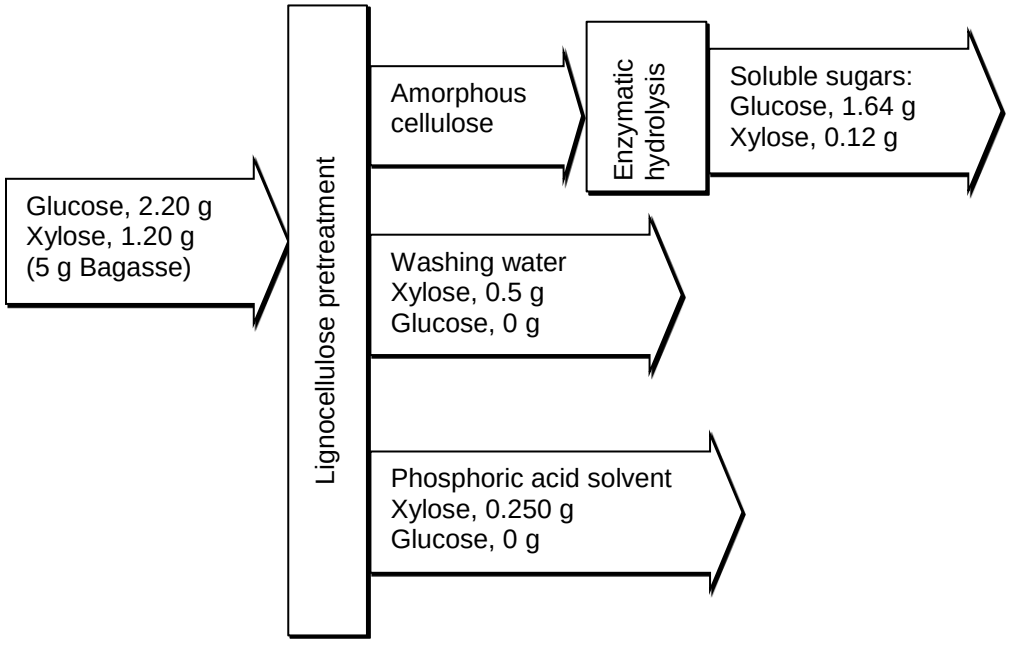

Fig. 5. The sugar mass balance of pretreated 5 g bagasse under condition I

The highest xylose content of 0.5 g was found in the washing water, and 0.25 g of xylose was dissolved in the acetone supernatant, which indicated most of the xylose in bagasse hemicellulose was released. The other 0.12 g of xylose was contained in the residue. Most of the glucose was retained in the amorphous residue.

A Proposed Integrated Biorefinery System for Pretreatment and Subsequent Platform Chemicals Preparation

The previous analysis of the effect of pretreatment condition on biomass fractionation illustrated that the structure of cellulose was damaged by concentrated phosphoric acid digestion; hemicellulose and part of lignin were separated from the residue. Acetone was used to extract lignin and remove most of phosphoric acid. The remaining bagasse was separated to residue with high cellulose content and water-soluble xylo-oligosaccharides through simple water washing.

The phosphoric acid and acetone can be recycled and used in the subsequent platform preparation procedures. The coupling process of the pretreatment and the subsequent conversion of xylo-oligosaccharides and cellulose is shown in Fig. 6. After step 2 of acetone extraction, the acetone supernatant was separated and recovered through centrifugation. Through liquid/solid separation using a separating funnel, lignin was recovered. The remaining solution was rich in phosphoric acid and contained approximately 20 wt% water-soluble xylo-oligosaccharides, as shown in step 4. After separation of the acetone supernatant, the remaining residue was washed with DI water, shown in step 3. The washing water contained phosphoric acid and 60% to 70% of water-soluble xylo-oligosaccharides, as shown in step 5. The water solutions of step 4 and step 5 can be combined to take full advantage of phosphoric acid to catalyze xylo-oligosaccharides to produce furfural. Due to the severe structural damage and removal of hemicellulose and part of lignin, the amorphous cellulosic residue was easy to prepare platform chemicals through acidic hydrolysis, and can also be used for glucose production through enzymatic hydrolysis.

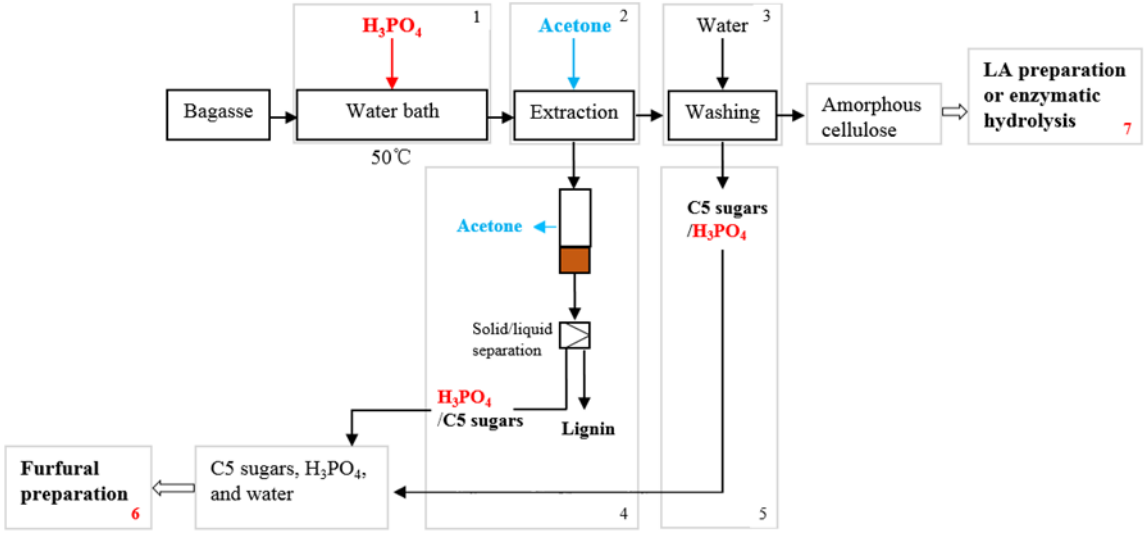

Fig. 6. A Proposed sketch of a biorefinery system coupling pretreatment with subsequent platform chemicals preparation by phosphoric acid and acetone system

The water solutions of step 4 and step 5 were mixed as 1:1 (v:v) and then added into the tubular reactor. The mixture was reacted at 180 °C for 60 min. The results are shown in Fig. 7. At the reaction beginning (time = 0 min), there were 2.35 g/L xylose, 0.22 g/L arabinose, and 0.02 g/L furfural. The concentrations of xylose and arabinose decreased sharply after 5 min. The maximum furfural concentration was 1.45 g/L at 45 min, which equaled to a furfural yield of 96.4 mol%. Then, the concentration of furfural began to decrease. The furfural concentration results showed that xylo-oligosaccharides were fully utilized and converted to furfural through catalysis of phosphoric acid from pretreatment.

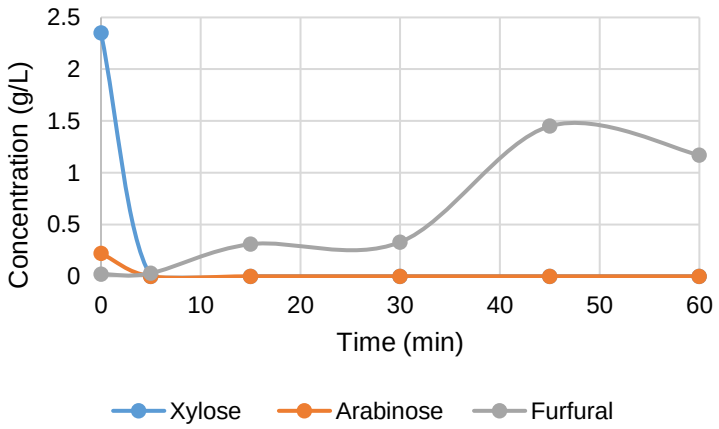

Fig. 7. Concentration trends of xylose, arabinose, and furfural; reaction conditions of 180 °C, 60 min, and pH = 1

The amorphous structure of the residue was advantageous for its conversion to high value-added compounds, such as LA, through acidic catalysis. In this study, there was a minimal phosphoric acid and acetone that remained in the pretreated residue. If the residue can be converted to LA catalyzed by the remaining phosphoric acid/acetone system, as step 7 in Fig. 6 shows, the economy of the whole biorefinery will be improved. The conversion of the model compound glucose to LA in the mixed solution of phosphoric acid and acetone was studied. As shown in Fig. 8a, it was found that at a low phosphoric acid loading (1 wt%) the conversion rate of glucose gradually increased, and glucose was not completely converted until 120 min of reaction. The yields of HMF first increased and then decreased, with the highest yield of 11.0% at 60 min. The yields of LA slowly increased, with the highest yield of 25.1% at 120 min. The addition of 0.5 wt% acetone facilitated the progress of the reaction, and the yield of LA slightly increased to 26.9% (Fig. 8b). Under the same reaction condition, when the concentration of phosphoric acid increased to 10 wt%, the reaction notably accelerated. The conversion rate of glucose quickly reached 100% in 30 min. The yields of LA first increased and then decreased, with the highest yield of 58.4% at 60 min, as shown in Fig. 8c. The addition of acetone (5 wt%) resulted in a slight decrease in the yields of HMF and LA, but the yields of LA were stable after reaching 50% at 30 min. The yields of formic acid (FA) were consistent with the yields of LA in all four conditions. Liu *et al*. (2018) investigated the hydrolysis properties of microcrystalline cellulose (MCC) in different aqueous polar aprotic solvents (acetone, THF, MIBK, GVL, etc.) with low severity sulfuric acid, and found acetone had better performance in hydrolysis of MCC. In their study, HMF yield (8-12%) was higher than that of LA (less than 2%), and obviously we have a much better LA selectivity and yield.

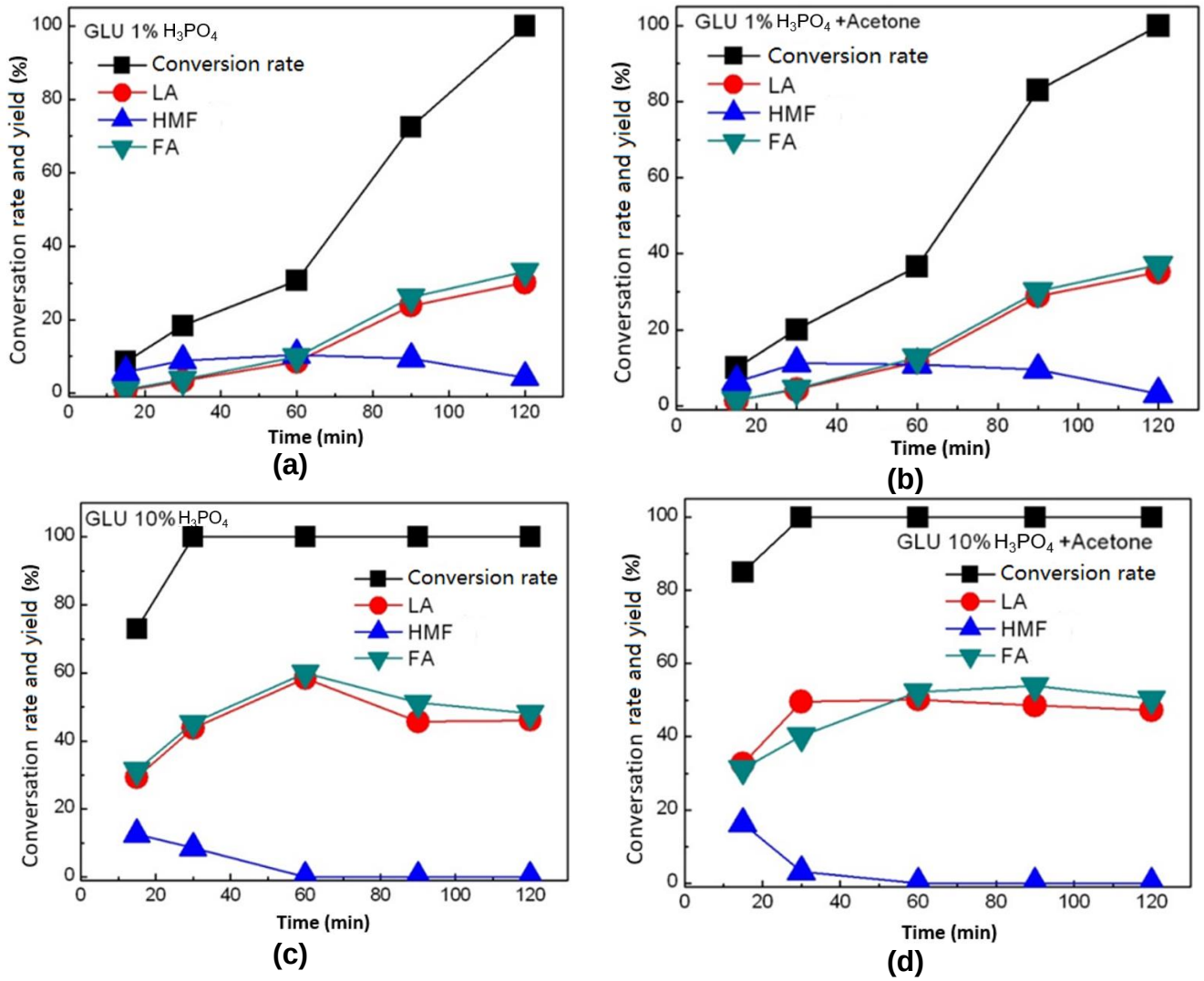

Fig. 8. Glucose conversation rates and yields of LA, HMF, and FA under different phosphoric acid/acetone systems; reaction conditions were 20 g/L glucose, 180 °C, and 60 min

The highest yield of LA was up to 58.4%, which proved the feasibility of preparing LA from pretreated residue. However, the concentration of phosphoric acid in the pretreated residue was low, which requires additional acid to obtain higher LA yields.

CONCLUSIONS

1. A biorefinery system combining the pretreatment of sugarcane bagasse and the subsequent two-step hydrolysis for furfural and levulinic acid (LA) generation was proposed. The catalysis system used in the pretreatment process and the platform chemical generation process were the same phosphoric acid/acetone system.
2. High furfural and LA yields were obtained. Meanwhile, acetone and part of jelly-like lignin were recovered.

3. Through a comprehensive study of the pretreatment, 72.5% of xylose and 74.5% of glucose compared to the theoretical amounts were obtained under the 85 wt% phosphoric acid digestion (8:1 acid/solid ratio) in 50 °C stirring water bath for 1 h followed by the addition of precooled acetone (-18 °C, 20:1 acetone/solid ratio). Their distribution was also revealed.

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