

# Influence of Acetone Co-Solvent on Furfural Production and Cellulose Retention from Lignocellulosic Biomass

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This research aimed to obtain furfural from sugarcane bagasse with most cellulose residue preserved by using the system of diluted phosphoric acid and co-solvent acetone. Based on concentrated phosphoric acid and acetone pretreatment, 78.2% of the hemicelluloses in the bagasse were depolymerized into water soluble xylo-oligosaccharides, covering the cellulose residue. Then, in the pure acetone medium, no furfural was produced when pretreated bagasse was catalyzed by phosphoric acid at low reaction temperature (80 °C). The degradation of pretreated bagasse was strongly accelerated by increasing reaction temperature (120 °C), while no furfural was obtained due to its condensation with acetone. Adding water (12 mL) effectively slowed this process, with 10.6% furfural yield and 54.4% furfural selectivity, but acetone showed an inhibiting influence on furfural production compared to pure water system, under atmospheric conditions. Surprisingly, furfural production in the acetone-water medium was improved significantly when the reaction was pressurized, using xylose or bagasse as the feedstock. In pressurized conditions, higher furfural yield, shorter reaction time, and lower cellulose degradation were observed in the acetone-water medium *versus* the totally aqueous medium. This provided the potential of producing furfural and hydrolysable cellulose residue in the acetone co-solvent media.

*Keywords:* Furfural; Acetone; Phosphoric acid; Sugarcane bagasse; Hydrolysable residue; Pressure

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## INTRODUCTION

The research on the platform chemicals prepared from lignocellulosic biomass has become a hot research topic in recent years (Werpy and Petersen 2004; Li and Luterbacher 2016). Hemicelluloses and cellulose are the main components of biomass fibers. The former can be converted into furfural, while the latter can be converted into 5-hydroxymethylfurfural (HMF) or levulinic acid.

Various acid/organic solvent combination strategies can effectively prepare platform chemicals, such as furfural, HMF, and levulinic acid. Adding immiscible organic solvents, such as methylbenzene (Burket and Sabesan 2012), methyl isobutyl ketone (Román-Leshkov *et al.* 2006; Zhang *et al.* 2013), and alkylphenols (Gürbüz *et al.* 2012), to the diluted acid solution, or adding miscible organic solvent, such as  $\gamma$ -valerolactone (GVL) (Dumesic *et al.* 2012) and tetrahydrofuran (THF) (Shi *et al.* 2013; Yang *et al.* 2013), to the saturated salt solution results in a biphasic medium. A major

advantage of this strategy is that the insoluble phase can extract the target platform chemicals from the aqueous phase, which prevents their further degradation and condensation. Another strategy is adding soluble organic solvents into the dilute acid solution, with the major advantage of changing the characteristic of the entire reaction system. For example, adding certain aprotic polar solvents, such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF), inhibits certain ring opening side reaction, which improves the yield of HMF (Román-Leshkov *et al.* 2006).

Although solvents like DMSO, DMF, and methylbenzene improve the conversion of carbohydrates to platform chemicals, their high boiling points have limited their application due to the difficulty of separating them from the target platform chemicals. Currently, organic solvents with low boiling points, that are easily recycled, and that are relatively non-toxic to environment, have received the most attention. THF is a typical low boiling point co-solvent applied in the generation of HMF, furfural, and levulinic acid from biomass conversion (Cai *et al.* 2013, 2014). As a widely used industrial organic solvent, acetone also has a low boiling point and is easily recovered. Qi *et al.* (2008) studied the dehydration of fructose to HMF in acetone-water mixtures in the presence of a cationic ion-exchange resin. The solvent media resulted in 73.4% yield of HMF, which represented a 94% conversion of the fructose, and their research revealed the higher portion of acetone in the mixture, the earlier and higher HMF yield. Bicker *et al.* (2003) found better selectivity of fructose conversion to HMF when using subcritical and supercritical acetone-water media with a higher proportion of acetone catalyzed by sulfuric acid. However, there are few reports about the production of furfural from C5 sugars in acetone media that are catalyzed by acids.

There are many reports about the simultaneous conversions of C5 and C6 sugars into platform chemicals. Shi (2015) reported the highest HMF and furfural yields were obtained from corn cob (*i.e.*, 47 mol % and 56 mol %, respectively), using the following conditions: 190 °C; 90 min; 2.4 wt % corn cob; 10:1 THF/NaHSO<sub>4</sub> solution; and 0.66 wt% catalyst loading. Cai *et al.* (2013) used dilute sulfuric acid-THF co-solvent medium (liquid-to-solid ratio of 20:1) to hydrolyze maple wood; the highest furfural and levulinic acid yields were 87 mol% and 32 mol%, respectively, with the following conditions: 170 °C for 40 min; 1 wt % sulfuric acid; and 3:1 THF/H<sub>2</sub>O media. When the authors increased the reaction temperature to 200 °C and the sulfuric acid content to 1.5 wt% without the THF co-solvent, the highest levulinic acid yield observed was 75 mol%, whereas the furfural yield was 0 mol%. One-pot methods reduce the reaction steps and shorten the total reaction time. However, due to the different structures and characteristics of cellulose and hemicelluloses in the cell wall, both the generation time and the generation difficulty of hemicellulose derived chemical (furfural) and cellulose derived chemicals (HMF and levulinic acid) are different. Therefore, the same high yields of these chemicals are hard to be achieved (Wyman *et al.* 2005). In addition, the subsequent separation of products has also been difficult. Cai *et al.* (2013) also indicated if the reaction media is single phase, the same high yields of furfural and HMF, or furfural and levulinic acid could be achieved by using a two-step method rather than a one-pot method due to the fact that furfural is less stable in the reaction medium.

This study adopted a novel catalyzing method by using acetone co-solvent media and phosphoric acid to directionally convert hemicellulose into furfural with the retention of cellulose. Aldol condensation of acetone and furfural catalyzed by alkaline catalysts is a very important procedure in the conversion of carbohydrate feedstocks to liquid alkanes for jet fuel production (Barrett *et al.* 2006; Chheda and Dumesic 2007). However, there

has been little research about the influence of acetone on furfural production from xylose or biomass catalyzed by acidic catalysts. This study investigated the effect of co-solvent acetone on furfural production from sugarcane bagasse catalyzed by phosphoric acid, under the different conditions of temperature, acid concentration, water amount, and pressure. To better observe the influence of co-solvent acetone on furfural production from bagasse hemicellulose under the low and medium temperatures, the concentrated phosphoric acid / acetone method was used (Sathitsuksanoh *et al.* 2009; Zhang *et al.* 2006, 2007; Rollin *et al.* 2011) to pretreat bagasse and to fractionate hemicellulose and cellulose. The phosphoric acid and acetone used in the pretreatment can also be used in the subsequent reaction. Under the pressurized condition, acetone can effectively improve furfural production and preserve cellulose residue. Besides, the application of acetone also benefits for water saving and easy recycling.

## EXPERIMENTAL

### Materials

Chemical reagents, such as phosphoric acid (85 wt%, Tianjin Fuyu Fine Chemical Co.Ltd.), acetone (Tianjin Damao Fine Chemical Co. Ltd.), D-xylose (Shanghai Yuanju Biotechnology Co. Ltd.), and glucose (Tianjin Damao Fine Chemical Co.Ltd.) were of analytical grade. Furfural (Aladdin Industrial Corporation), 5-hydroxymethylfurfural (Aladdin Industrial Corporation), and levulinic acid (Sigma-aldrich Co.Ltd.) were of spectrographic grade.

Sugarcane bagasse (*i.e.*, bagasse) was collected from the Guangxi Province of China. After machine milling, it was screened through 40- and 60-mesh screens, and then dried overnight in an oven at 45 °C.

### Concentrated Phosphoric Acid and Acetone Pretreatment

Bagasse feedstock (1 g) and concentrated phosphoric acid (8 mL) were placed in a pear-shaped bottle. A stirring bar was inserted for mechanical agitation, and the bottle was sealed with a rubber stopper. The bottle was then put in a 50 °C water bath. Acetone (20 mL) was added after 45 min of the phosphoric acid treatment. The mixture was then centrifuged at 4000 rpm for 20 min to separate the supernatant and the residue. Fresh acetone (20 mL) was added to wash the residue again, and this supernatant was mixed with the previously obtained supernatant from centrifugation. The optimum time for the phosphoric acid treatment was determined based on the analyses of the reaction products.

### Reactions of Pretreated Bagasse Conversion without Additional Pressure

*Reactions under residual phosphoric acid and fresh acetone at 80 °C for 10 or 30 min*

Fresh acetone (20 mL) was added to the residue after pretreatment. The bottle was sealed with a glass stopper, tightly wrapped with sealing film, placed into an 80 °C water bath for 10 or 30 min, and then cooled in an ice-water bath. For comparison, experiments with 20 mL of fresh ethanol were also tested. Solids were separated from the reaction liquors by vacuum filtration at room temperature through qualitative filter papers (General Electric (China) Co., Ltd., Shanghai, China; Double Ring Series), and washed with room temperature water. The washing water and reaction liquors were analyzed by high performance liquid chromatography (HPLC) respectively, while the reaction liquors

were further analyzed by gas chromatography-mass spectroscopy (GC-MS) (described below).

*Reactions under original phosphoric acid and acetone at 80 °C for 60 min*

After pretreatment, the pretreated bagasse with its pretreatment medium of acetone and phosphoric acid was maintained in the bottle. The bottle was sealed with a glass stopper, tightly wrapped with sealing film, placed in an 80 °C water bath for 60 min, and then cooled in an ice-water bath. The separation of solids and liquors, and the analyses of washing water and reaction liquors were implemented as described earlier for the reactions with fresh acetone addition.

*Reactions under original phosphoric acid and acetone at 120 °C for 30 min*

The pretreated bagasse with its pretreatment medium of acetone and phosphoric acid was transferred to a 50 mL hydrothermal reactor with a PTEE lining (Shanghai Yaote Instrument Co., Ltd., Shanghai, China), and heated by the electric heating jacket at 120 °C for 30 min. After the reaction, water was directly added to the slurry, and the solids separated by vacuum filtration at room temperature after stirring. The washing water was analyzed by HPLC and GC-MS.

*Reactions under original phosphoric acid and acetone diluted by water at 120 °C and 170 °C*

Bagasse was pretreated with phosphoric acid without acetone co-solvent addition. After pretreatment, the entire mixture was transferred to the 50 mL hydrothermal reactor with PTEE lining with a certain amount of acetone and water, and heated by the electric heating jacket at 120 °C for 30, or 170 °C for 90 min. After the reaction, the solids were separated from reaction liquors by vacuum filtration at room temperature, and the reaction liquors were analyzed by HPLC.

The reaction of pure xylose (0.2052 g, which was equal to the xylose content of bagasse hemicellulose) was conducted at similar treatment conditions. This was done to compare to the bagasse conversion at 170 °C.

### **Pressurized Reactions of Bagasse Conversion**

Pressurized reactions were conducted in a 100 mL autoclave reactor (Anhui Kemi Machinery Technology Co., Ltd., Anhui, China; Model MS-100-C276) equipped with a double helical ribbon and screw impeller, which rotated at 500 rpm. Reagent xylose and bagasse reactions were both loaded with 2 wt% xylose loading and 0.17% phosphoric acid loading (based on liquid volume), while no acetone was used or acetone was used at a 7:3(v:v) acetone-to-water ratio. Prior to each reaction, the autoclave was pressurized to 1.5 MPa with nitrogen. Temperatures for reagent xylose and bagasse pressurized reactions were 150 °C. All reactions were maintained at 150 °C ( $\pm 2$  °C) using programmed temperature controllers where the reactor temperature was measured directly by an in-line thermocouple. After the completion of each pressurized reaction, the reactor was cooled rapidly with cold air, and the solids were separated from the liquor by vacuum filtration at room temperature. The separated liquors were then analyzed by HPLC.

## Analytical Methods

The composition of the bagasse feedstock was determined by using the procedures of Sluiter *et al.* (2008), specifically LAP-002 to evaluate the carbohydrates in the biomass and LAP-003 to evaluate the acid-insoluble lignin. In certain situations, secondary hydrolysis with 4% sulfuric acid was required to hydrolyze the xylo-oligosaccharides into monosaccharides. The results of these analyses revealed that the biomass was composed of 38.28% glucan (42.53% glucose), 18.06% xylan (20.52% xylose), and 24.77% Klason lignin, all expressed on a dry weight basis.

The monosaccharides, aldehydes, and levulinic acid were detected and quantified using HPLC (Waters Corp., Milford, MA, USA; Model 2695) equipped with a Shodex sugar SH-1011 column coupled with a refractive index detector (Waters Corp.; Model 2414) and a photodiode array detector (Waters Corp.; Model 2998). The mobile phase employed with the column was 0.005 M H<sub>2</sub>SO<sub>4</sub>; 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 levulinic acid 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.

Qualitative analysis of the liquid product was performed using a GC-MS instrument (Hewlett-Packard (Agilent Technologies), Santa Clara, CA, USA; GC Model HP 5890 and MS Detector Model HP 5972A) equipped with an INNOWAX capillary column (30 m × 0.32 mm × 0.25 µm). The oven temperature was maintained at 60 °C for 5 min, then ramped to 240 °C at a 10 °C·min<sup>-1</sup> rate, and held at 240 °C for 28 min.

## Equations

The xylose conversion rate ( $X_c$ ), furfural selectivity ( $F_s$ ), and furfural yield ( $F_y$ ) were calculated as follows,

$$X_c = (\text{moles of xylose reacted}) / (\text{moles of initial xylose}) \times 100\% \quad (1)$$

$$F_s = (\text{moles of furfural produced}) / (\text{moles of xylose reacted}) \times 100\% \quad (2)$$

$$F_y = X_c \times F_s \quad (3)$$

where *moles of initial xylose* is the reagent xylose used or the xylose contained in the hemicelluloses of the bagasse biomass.

## RESULTS AND DISCUSSION

### Results of Concentrated Phosphoric Acid and Acetone Pretreatment

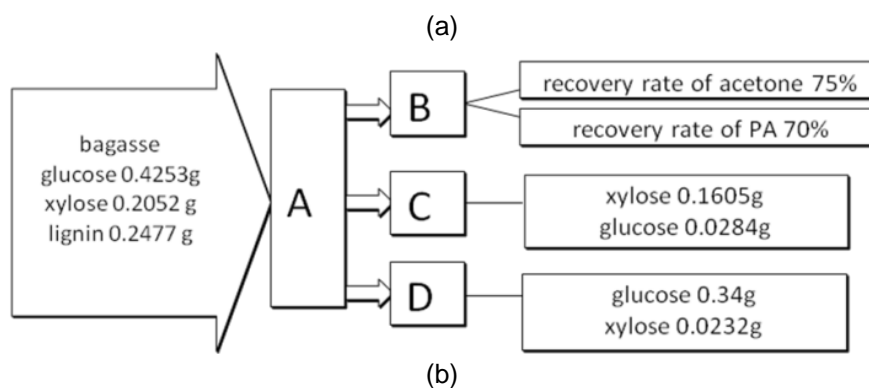
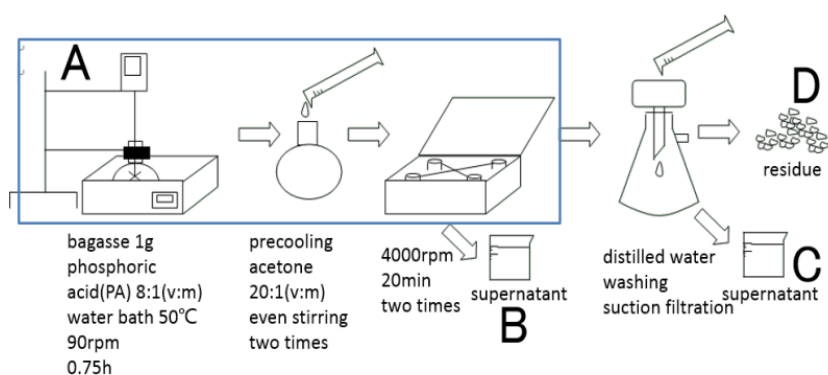
The purpose of each step of concentrated phosphoric acid and acetone pretreatment is shown in Table 1, based on the research of Zhang *et al.* (2007). Phosphoric acid digestion is the most important step, which converts most of xylan in hemicelluloses as xylo-oligosaccharides and other xylan remaining in pretreated residues.

The detailed pretreatment procedures and compositional analyses of pretreatment products are shown in Fig. 1. The detailed recovery methods of acetone and phosphoric acid are not shown.

It was observed that 0.1605 g xylose was generated when the material was treated with 4% sulfuric acid, which indicated that most of xylan in hemicelluloses was degraded to xylose-oligosaccharides; this accounted for 78.22% of the xylose in the bagasse biomass. The majority of cellulose (79.94% of the glucose in the bagasse) was remained in the residue as an amorphous mass.

**Table 1.** Purpose of Each Step of Concentrated Phosphoric Acid and Acetone Pretreatment

Steps	Cellulose	Hemicellulose	Lignin	Others
Phosphoric acid digestion	Orderly destruction of hydrogen bonding; weakly hydrolysis of cellulose to low degree of polymerization fragments	Hydrolysis of xylan in hemicelluloses to xylo-oligosaccharide; removal of acetyl groups of hemicellulose to produce acetic acid	Cleavage of bonds between lignin and sugar chains	—
Acetone extraction	Precipitation	Extraction of acetic acid	Solubilization of free lignin	Wash out most phosphoric acid and acetone
Water washing	—	Wash out xylo-oligosaccharides	—	Wash out residual phosphoric acid and acetone
Residuals	Nearly all cellulose in amorphous form	Trace in the residue	Part of lignin	



**Fig. 1.** Schematic diagram (a) and full composition analysis (b) of the concentrated phosphoric acid (PA) and acetone pretreatment

### Analysis of Products from Sugarcane Bagasse Conversion in Phosphoric Acid and Acetone System without Water and Additional Pressure

There was 89.5% of xylose (as water-soluble xylo-oligosaccharides and xylan in the solid) in the bagasse residue after the pretreatment step; only 10.5% was removed with acetone extraction. A small amount of phosphoric acid remained with the pretreated bagasse solids, which had a pH of approximately 1.2. Initially, the experiments were conducted by adding acetone to the residue to examine its influence on furfural production. Reactions under moderate temperature (80 °C) and short reaction time (10/30 min) were first approached.

The supernatant produced after the pretreatment reaction was separated from the residue by centrifugation. However, the HPLC analysis indicated that there was no furfural or monosaccharides in the supernatants of acetone or ethanol. When the residue was washed with water, a small amount of xylose was detected in the washing liquid with no furfural, glucose, 5-HMF, or levulinic acid (Table 2 (columns a1, a2, a3 and a4)). Treating a2 solution with 4% sulfuric acid resulted in 0.1011g xylose in the hydrolysate, which indicated that 63% of xylo-oligosaccharides were not involved in the reaction. It was anticipated that more xylo-oligosaccharides would degrade to xylose after a 30 min treatment without furfural production.

**Table 2.** HPLC Results of Supernatant and Washing Liquid of Reaction Residue over Different Conditions without Water

Yields	Supernatant	Washing Liquid					
	b	a1	a2	a3	a4	b	c
Furfural (%)	trace	—	—	—	—	trace	0.23
Xylose (%)	9.50	0.73	1.71	0.49	0.97	22.32	—
Glucose (%)	—	—	—	—	—	—	22.92
5-HMF (%)	—	—	—	—	—	—	—
Levulinic acid (%)	—	—	—	—	—	—	2.55

a1: Reaction under residual phosphoric acid and fresh acetone at 10 min; a2: Residual phosphoric acid and fresh acetone, 30 min; a3: Residual phosphoric acid and fresh ethanol, 10 min; a4: Residual phosphoric acid and fresh ethanol, 30 min; b: Original phosphoric acid and acetone, 80 °C, 60 min; and c: Original phosphoric acid and acetone, 120 °C, 30 min

The GC-MS analyses of acetone supernatants (30 min) and ethanol supernatants (30 min) were similar (Fig. S1, a2 and a4). It was found that acetic acid accounted for 39.0% (Table 3 (column a2)) and 54.7% (Table 3 (column a4)) of the relative content of compounds in the supernatants. Acetic acid was derived from the acetyl acetate of hemicelluloses. Because most acetic acid had been dissolved and removed with the acetone supernatant during pretreatment, the high amount of acetic acid in the reaction solution indicated that the yields of chemicals from the pretreated bagasse, such as furfural, HMF, and acids were low. In addition to acetic acid, propionic and butyric acid were also detected (Table 3 (columns a2 and a4)). At the reaction condition of acetone for 30 min (Table 3, columns a2), the acetone condensation products 4-hydroxy-4-methyl-2-pentanone and methyl isobutenyl ketone were detected. A trace amount of 4-hydroxy-4-methyl-2-pentanone was detected when the reaction was carried out with residual phosphoric acid and fresh ethanol (Table 3 (column a4)); this is likely attributable to the condensation of residual acetone from the pretreatment. In addition, a small amount of

1,2:3,5-di-*O*-isopropylidene- $\alpha$ -D-xylofuranose was generated in one of the experimental runs (Table 3 (column a2)).

Because the experimental results obtained at 80 °C and 30 min were not ideal, experiments under higher phosphoric acid concentration and longer reaction time were considered. Therefore, an experiment was conducted at 80 °C for a longer time (60 min) while maintaining the acetone supernatant after pretreatment.

The results observed from this experiment were clearly different. There were 9.50% xylose, trace furfural, and no other low molecular weight organic acids (Table 2 (column b) and Table 3 (column b)) in the acetone supernatant. This observation demonstrated that higher acid concentration during the reaction benefited xylo-oligosaccharides degradation and furfural production. Methyl isobutenyl ketone and 4-hydroxy-4-methyl-2-pentanone were detected in the acetone supernatant (Fig. S1, c), which accounted for 31.0% and 26.9%, respectively, of the total product components. This was more than that obtained in residual phosphoric acid-acetone system, which indicated that more acetone condensation occurred while higher phosphoric acid concentration was applied (Table 3 (column b)).

Because there were low yields of furfural during the reaction with residual and original phosphoric acid at 80 °C, experiments under higher acid concentration and higher temperature were now considered. When the reaction was conducted at 120 °C for 30 min, black and sticky products were formed; they were washed by water, and this washing liquid was analyzed, as shown in Table 2 (column c). All xylo-oligosaccharides were degraded. However, there was no xylose detected; the furfural yield was only 0.23%. Furthermore, 22.9% glucose was detected, indicating there was depolymerization of bagasse cellulose under this reaction condition. A small amount of glucose degradation products, glycolic acid, and levulinic acid were also detected. This observation indicated the degradation of amorphous cellulose to glucose, which was then degraded to levulinic acid. Furthermore, acetone condensation products accounted for approximately 50% of the total products (Table 3 (column c)).

**Table 3.** GC-MS Analyses of Main Components in Supernatants from Different Treatment Conditions without Water

Component Name	Peak Area Ratio (%)			
	a2	a4	b	c
Methyl isobutenyl ketone	3.52	—	30.96	13.39
4-hydroxy-4-methyl-2-pentanone	4.17	0.84	26.93	36.00
Acetic acid	38.95	54.68	9.11	11.74
Propanoic acid	5	5.91	—	—
Butanoic acid	5.81	5.29	—	—
1,2:3,5-di- <i>O</i> -isopropylidene- $\alpha$ -D-xylofuranose	3.94	—	—	—

a2: Residual phosphoric acid and fresh acetone, 30 min; a4: Residual phosphoric acid and fresh ethanol, 30 min; b: Original phosphoric acid and acetone, 80 °C, 60 min; and c: Original phosphoric acid and acetone, 120 °C, 30 min



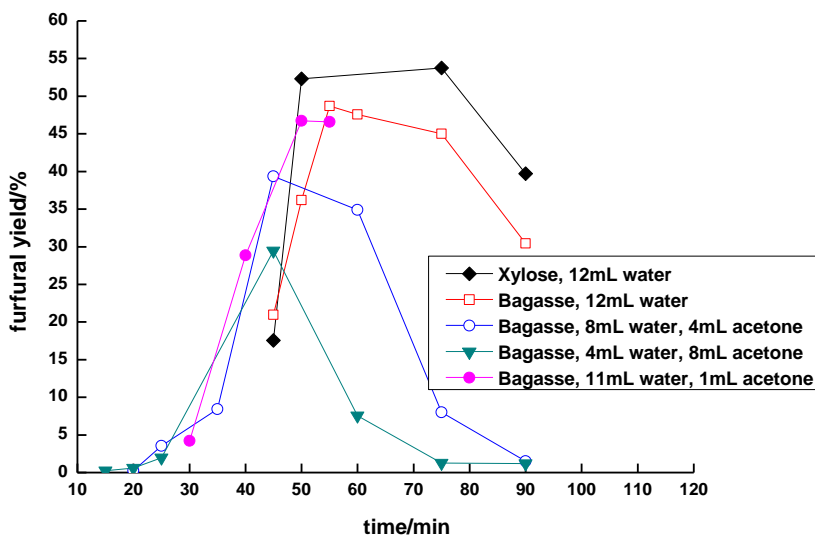
## Furfural Production from Sugarcane Bagasse Conversion in Phosphoric Acid and Acetone System Diluted by Water

The previous results indicated that the conversion of xylo-oligosaccharides in phosphoric acid-acetone media was sensitive to reaction temperature; thus, subsequent reactions were diluted by water. It was found that the furfural yield and furfural selectivity was 13.2% and 54.6%, respectively, in the reaction system with 12 mL of water, as shown in Table 4. In order to increase the furfural yield, lower amounts of solvents were considered to increase the acid concentration. A furfural yield of 20.4% was obtained by using 4 mL of acetone and 8 mL of water. As a control, an experiment where 12 mL of water was investigated for furfural yield; however, the furfural yield was higher (25.3%), which indicated that acetone reduces the yield of furfural obtained.

**Table 4.** Furfural Results from Bagasse Conversion under the Same Phosphoric Acid-Acetone-Water Medium or Phosphoric Acid-Water Medium

Amount (mL)		$X_c$ (%)	$F_s$ (%)	$F_y$ (%)
acetone	water			
20	12	24.22	54.62	13.23
4	8	38.78	52.47	20.35
0	12	43.99	57.57	25.32

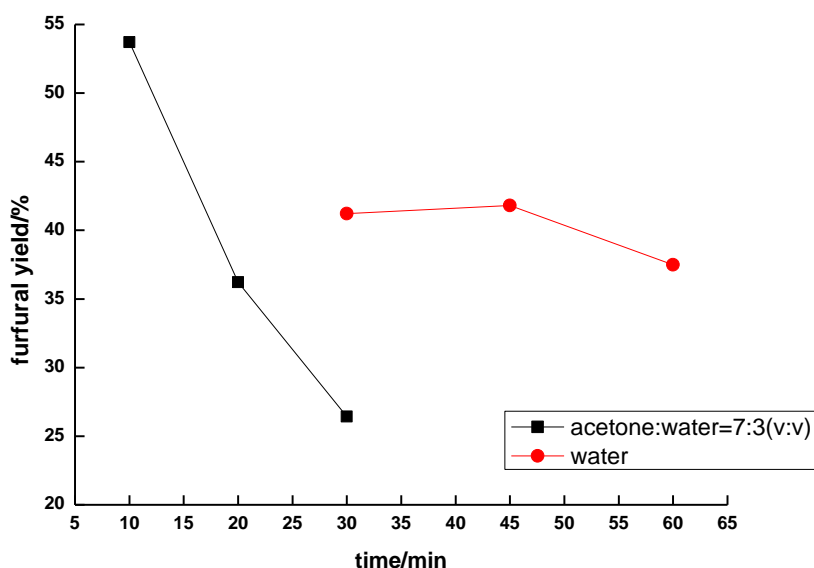
The influence of acetone on furfural production at higher temperature was investigated. Experiments were conducted in which the reaction temperature approached 170 °C using bagasse or reagent xylose as feedstock. These experiments also used different water-to-acetone proportions as the reaction media. It was observed that the highest furfural yield (53.7%) was obtained at 75 min in a totally aqueous water medium using xylose as substrate. The highest furfural yield of 48.7% was obtained with bagasse substrate at the same conditions for 55 min. When 1 mL water was replaced by 1 mL acetone, the highest furfural yield was a bit lower, but it occurred at shorter reaction time (Fig. 2). Similarly, as more of the water is replaced by acetone, the highest furfural concentration levels decreased, though there was a decrease in the time period during which there was significant furfural production.



**Fig. 2.** Comparisons of furfural yields in the conversions of xylose and bagasse using phosphoric acid-acetone-water media with different acetone-to-water ratios

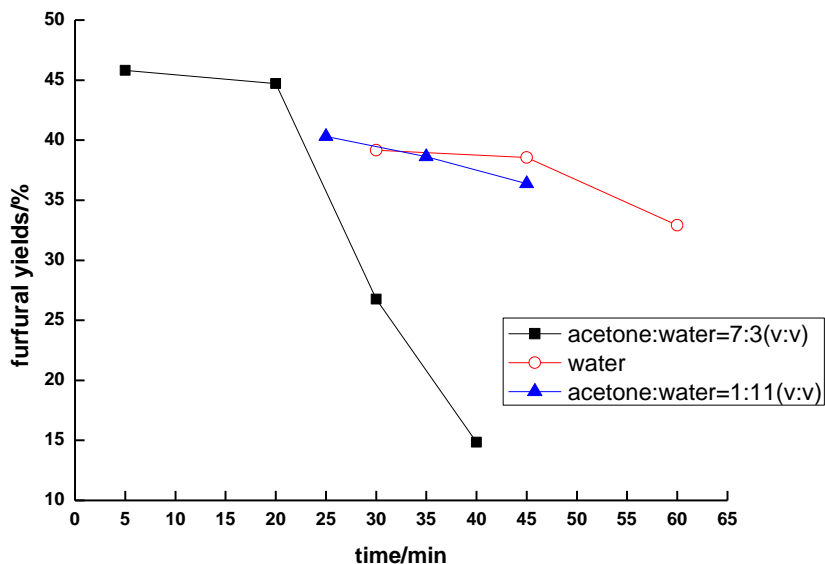
### Improvement of Furfural Production and Cellulose Retention by Pressurized Phosphoric Acid and Acetone System Diluted by Water

The previous results showed that acetone tended to inhibit furfural production without additional pressure. Surprisingly, at pressurized conditions (under a nitrogen atmosphere), the furfural yield reached 53.7% at 10 min in the acetone-water medium (7:3, v:v), whereas it was just 41.8% at 45 min for the water medium (Fig. 3). This result was very different from the reactions conducted without additional pressure where acetone inhibited furfural production.



**Fig. 3.** Furfural yields with two reaction media at 1.5 MPa with a nitrogen atmosphere

The reactions of bagasse carried out under pressurized reaction system and 150 °C are shown in Fig. 4. The highest furfural yield in the acetone-water medium (7:3, v:v) was higher than that in the pure water media (45.8% vs. 39.2%, respectively). In addition, the presence of acetone in the medium significantly shortened the reaction time needed to reach these production levels. In order to further determine the improvement affect of acetone for furfural yield in the pressurized reaction system, a little content of acetone was used in the acetone-water medium (1:11, v:v). It was found the highest furfural yield was higher, and generation time shortened.



**Fig. 4.** Furfural yields of bagasse conversion under three reaction media at 1.5 MPa with a nitrogen atmosphere

There was 1.15% HMF generated when the highest furfural yield was obtained in the acetone-water medium (7:3, v:v), but no levulinic acid was detected. Moreover, there was still no levulinic acid generated for 20 min. In the pure water media, 1.31% levulinic acid was obtained at 30 min, and levulinic acid yields continued increasing to 7.32% at 45 min. This observation indicated that the improvements of furfural production and cellulose retention could be achieved in the pressurized phosphoric acid-acetone-water system compared to the reaction in the system without acetone.

**Table 5.** Results of Yields of HMF and Levulinic Acid in Bagasse Conversion in Two Types of Phosphoric Acid-Acetone-Water Media at 1.5 MPa under a Nitrogen Atmosphere

Time (min)	Reaction Medium	HMF yield (%)	Levulinic acid yield (%)
5	Acetone: water = 7:3	1.15	0
20	Acetone: water = 7:3	0.67	0
30	Water	0.20	1.31
45	Water	0.68	7.32
60	Water	1.11	3.90

Table 6 listed the comparison between results proposed and previous results already published. Simultaneous production of furfural derived hemicellulose and HMF (or levulinic acid) derived from cellulose was studied by researchers, while it was hard to obtain the same high level of yields.

**Table 6.** Comparison of Different Acid/Organic Solvent Systems

Feedstock	Main goals	Reaction systems	Furfural yield (%)	HMF yield (%)	Levulinic acid yield (%)	Cellulose yields (%)	Ref.
Corn cob	production of furfural and 5-HMF	NaHSO <sub>4</sub> -THF-H <sub>2</sub> O, biphase, 190 °C	56	47	-	-	(Shi, 2015)
Maple wood	production of furfural and LA	H <sub>2</sub> SO <sub>4</sub> -THF-H <sub>2</sub> O, single phase, 170 °C	87	-	32	-	(Cai <i>et al.</i> 2013)
Corn stover	production of furfural and LA	H <sub>2</sub> SO <sub>4</sub> -GVL-H <sub>2</sub> O, single phase, 170 °C	56	-	61	-	(Alonso <i>et al.</i> 2013)
Sugarcane bagasse	production of furfural and preservation of cellulose	H <sub>3</sub> PO <sub>4</sub> -acetone-H <sub>2</sub> O, single phase, 150 °C	46	1.15	0	78	

This study aimed to generate furfural with cellulose retention from sugarcane bagasse. By using pressurized phosphoric acid-acetone-water media, 46% furfural was generated from hemicellulose with 78.2% cellulose preserved, which indicated that research purpose of directional conversion of hemicellulose into furfural with more cellulose preserved could be achieved.

## CONCLUSIONS

1. Acetone addition to the reaction medium improved furfural production and preserved more hydrolysable cellulose residue from sugarcane bagasse that is catalyzed by phosphoric acid at pressurized conditions *versus* a purely aqueous media.
2. Without water in the reaction medium, the conversion of bagasse in the phosphoric acid and acetone system is very sensitive to the reaction temperature, which can result in low furfural yields and significant levels of condensation products with acetone.
3. Acetone addition to the reaction medium shortened the furfural production time when using a bagasse substrate; however, the yield decreased in the diluted phosphoric acid system at atmospheric pressure.
4. This research indicated that pressurized acetone and diluted acids reaction media have potential to produce furfural and hydrolysable cellulose residue from lignocellulosic biomasses with high furfural yield, low water usage, and easy recovery of hydrolysable products.

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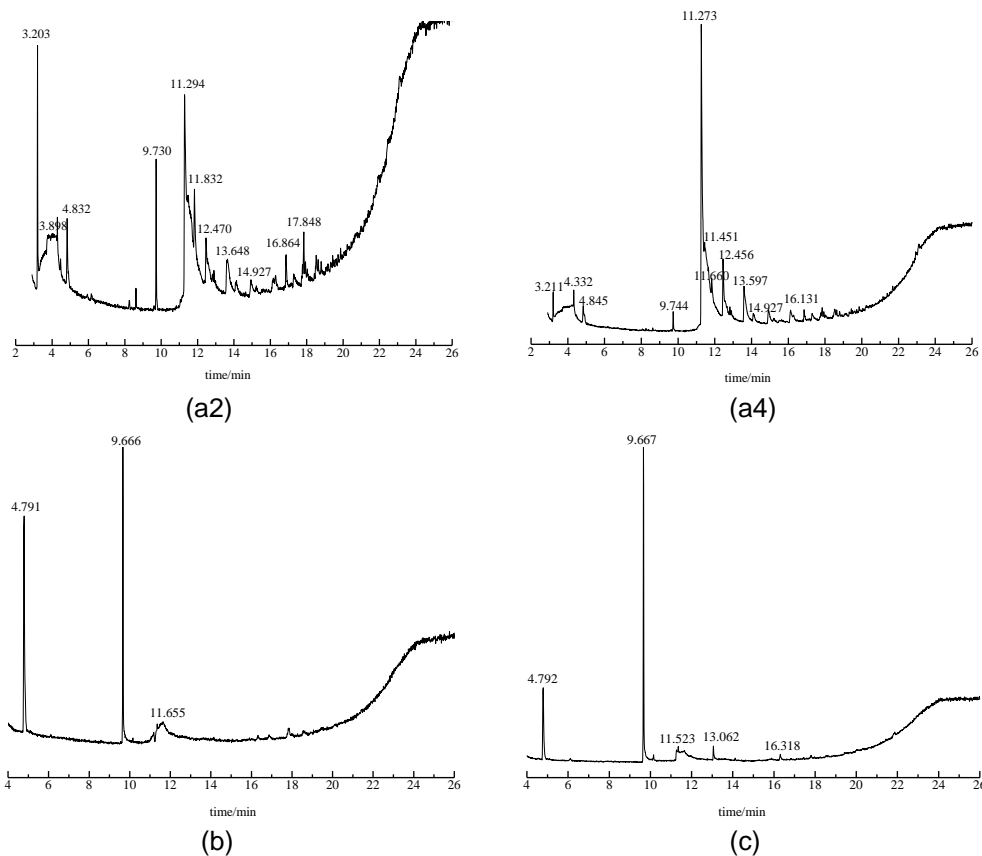
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## APPENDIX



**Fig. S1.** GC chromatograms of supernatants at different conditions without an aqueous medium: (a2) residual phosphoric acid and fresh acetone, 30 min; (a4) residual phosphoric acid and fresh ethanol, 30 min; (b) original phosphoric acid and acetone, 80 °C, 60 min; and (c) original phosphoric acid and acetone, 120 °C, 30 min