

# Efficient Production of Furfural from Corncob by an Integrated Mineral-Organic-Lewis Acid Catalytic Process

Suping Zhang,\* Junjie Lu, Miao Li, and Qinjie Cai

An M-O-L acid (mineral acid, organic acid, and Lewis acid)-catalyzed integrated process for furfural production from corncob was proposed to improve corncob conversion and furfural selectivity. First, the co-catalysts of sulfuric acid and acetic acid were investigated for their impact on furfural production. Sulfuric acid as a pretreatment catalyst was mixed with corncob before the experiment. Acetic acid, which is a byproduct of hemicellulose hydrolysis, was fed together with steam. The results showed that the cooperation of sulfuric acid and acetic acid decreased the total acid consumption dramatically.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was also investigated as a co-catalyst in an effort to enhance the conversion of xylose to furfural and decrease furfural degradation. The integrated catalytic process achieved the highest furfural yield of 68.04% through the use of M-O-L acid under a reaction temperature of 180°C, 3v% acetic acid, 4.0 wt.% sulfuric acid of 0.6 mL/g liquid to solid ratio, and 5 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  per 100 g of biomass.

*Keywords:* Furfural production; M-O-L acid; Integrated catalytic process

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## INTRODUCTION

Lignocellulosic biomass, mainly composed of hemicellulose, cellulose, and lignin, is the most abundant renewable resource and is a promising feedstock for production in second-generation bio-fuel and biochemicals (Mamman *et al.* 2008; Oh *et al.* 2013). Furfural, derived from hemicellulose, is an important bio-based platform chemical with a wide variety of applications including plastics, pharmaceuticals, agrochemical, and conversion to bio-fuel (Zhang *et al.* 2014; Park *et al.* 2016; Peleteiro *et al.* 2016). Currently, furfural is industrially produced from agro-based biomass, such as corncob or bagasse, by the acid hydrolysis of hemicellulose (mainly xylose) and by the dehydration of pentoses (Agirrezabal-Telleria *et al.* 2014).

Mineral acids such as  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  are effective catalysts used in industrial furfural production (Herrera *et al.* 2004; Agirrezabal-Telleria *et al.* 2014). Sulfuric acid is an effective catalyst for the depolymerization of biomass by the cleavage of glycosidic bonds under the action of hydrogen ion to oligomeric sugars and pentoses (Kumar *et al.* 2015). Under the action of hydrogen ions, the long chain of hemicellulose contained in lignocellulosic biomass is hydrolyzed to xylose and other monosaccharides, while cellulose and lignin fractions remain almost unreacted. Xylose is dehydrated to furfural, which is continuously stripped out by steam to minimize its loss through side-reactions of degradation or condensation. It is necessary to increase temperature and acid concentration and reduce reaction time to enhance furfural yield (Avci *et al.* 2013). Typical reaction conditions of industrial furfural production are 5 wt.% sulfuric acid, an acid solution to

lignocellulosic mass ratio of 2:1, temperature of approximately 180 to 200 °C, and reaction time of 2 to 3 h, with maximum furfural yields between 45% and 50% of the potential (Mao *et al.* 2012). Of course, the acid corrosion problem is inevitable, and the furfural yield has room for improvement.

Compared with mineral acids, organic acids have much lower corrosion and are easier to separate and reuse. Organic acids can partially dissociate into hydrogen ions to accelerate the delignification and hydrolysis of hemicelluloses (Guenic *et al.* 2015; Xu *et al.* 2015). Acetic acid is an organic acid that is the byproduct of hemicellulose hydrolysis; it causes less corrosion than sulfuric acid or hydrochloric acid. However, because the quantity of hydrogen ions ionized is limited, organic acids should be used as co-catalysts and in high concentration for furfural production. Abad *et al.* (1997) used HCl-catalyzed processing in 95% acetic acid solutions containing 0.2% to 0.4% HCl for furfural production. A process of co-catalyzed hydrolysis of corncob with acetic acid and FeCl<sub>3</sub> was evaluated, and a maximum furfural yield of 67.89% was obtained within a time period of 30 min at 3% of acetic acid, 20 mM of FeCl<sub>3</sub>, and 180 °C reaction temperature (Mao *et al.* 2012).

Lewis acids can be used to isomerize xylose to xylulose (Choudhary *et al.* 2012; Bruce *et al.* 2016). Lewis acids, mostly metal chlorides, accelerate furfural formation by contributing metal cations and Cl<sup>-</sup> ions (Marcotullio and De 2010). Metal chlorides alleviate corrosion problems caused by mineral acids and they accelerate xylose dehydration into furfural *via* the formation of xylulose, which is easier to dehydrate into furfural (Yang *et al.* 2012). Among the metal chlorides, the effect of trivalent metal chlorides is more remarkable (Choudhary *et al.* 2012; Zhang *et al.* 2014). Catalytic effects of many acidic heterogeneous catalysts including NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, MnCl<sub>2</sub>, and CuCl<sub>2</sub>·2H<sub>2</sub>O have been studied; the results showed that FeCl<sub>3</sub>·6H<sub>2</sub>O displayed superior performance (Mao *et al.* 2013). Fe<sup>3+</sup> had a relevant catalytic effect on the reaction of xylose (Zhi *et al.* 2015). Furthermore, the reaction of xylose catalyzed by FeCl<sub>3</sub>·6H<sub>2</sub>O was much faster than reactions with other chlorine salts (Marcotullio and De 2010). The chloride ions enhanced furfural formation from D-xylose in dilute aqueous acidic solutions (Liu *et al.* 2006; Mao *et al.* 2008; Mao *et al.* 2013; Xu 2016).

Furfural is active because of its furan ring and aldehyde group. Side reactions are the main cause of low furfural yield (Choudhary *et al.* 2012; Bruce *et al.* 2016). Though the catalyst enhances the reaction rate, the rate of side reactions is also enhanced (Jing and Lu 2007). These included the decomposition of furfural into formic acid and the condensations of furfural with furfural, xylose, and lignin-related phenolic compounds (Brazdauskas *et al.* 2016). Over the past decade, studies have been conducted on developing a more economical and efficient process for industrial furfural production from lignocellulosic biomass (Bamufleh *et al.* 2013).

From a practical viewpoint, M-O-L acid (mineral acid, organic acid, and Lewis acid) was used in this work to improve the conversion ratio of corncob and simultaneously increase the furfural yield. First, with using sulfuric acid, the biomass of hemicellulose was depolymerized to pentose (mainly xylose). However, the consumption of sulfuric acid was reduced with the assistance of acetic acid, which was produced as a byproduct to achieve a specified production of furfural. Secondly, under the action of a Lewis acid (FeCl<sub>3</sub>·6H<sub>2</sub>O), xylose was isomerized to xylulose. Xylulose was dehydrated to furfural under the action of Brønsted acidity. This method of dehydration resulted in a much higher furfural yield than direct xylose dehydration.

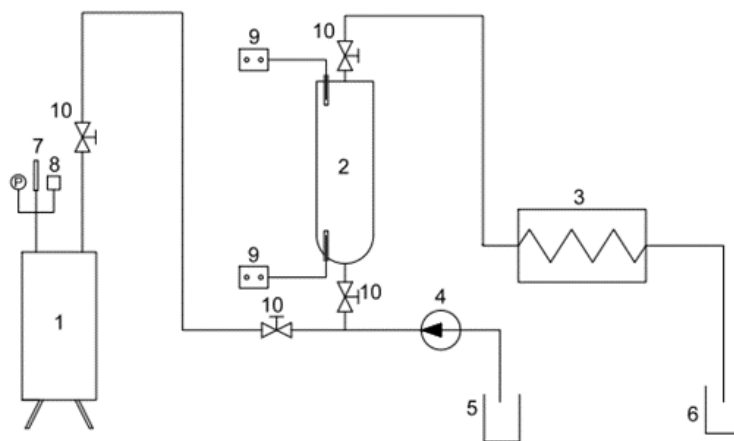
## EXPERIMENTAL

### Materials

Corncoobs were obtained from Hebei province, China. The materials were sieved to a size between 5 and 10 mm and then vacuum-dried at 105 °C to a constant weight.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was purchased from Sign pharm Chemical Reagent Co., Ltd. (Beijing, China).  $\text{H}_2\text{SO}_4$  and  $\text{CH}_3\text{COOH}$  were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. (Shanghai, China). Distilled water was used to prepare the solutions and dilute the samples.

### Equipment

The experiments were carried out in a percolating reactor made of stainless steel with an inner diameter of 90 mm and a volume of 1.5 L. A steam generator was connected with the reactor to generate steam continuously. The reactor and the steam generator, equipped with pressure sensors, were purchased from Zhengyuan Mechanical & Electrical Equipment Co., Ltd. (Shanghai, China). The pump used to inject  $\text{CH}_3\text{COOH}$  into the reactor was purchased from Guangzhou Royal Automation Systems Co., Ltd. (Guangzhou, China). The condensation system was used for condensing furfural *via* cold water. The instrument used in experiments is shown in Fig. 1.



**Fig. 1.** Schematic diagram of conversion corncoobs into furfural. (1) Steam generator; (2) reactor; (3) reflux condensation device; (4) pump; (5) containers of acetic acid; (6) product collection containers; (7) pressure reducing valve; (8) pressure control instrument; (9) thermocouple and temperature displays; (10) control valve; P, pressure gage

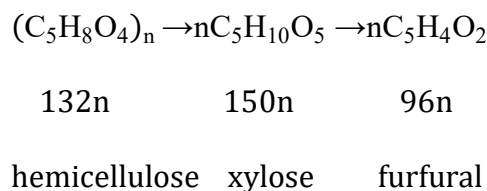
### Experiment Procedure

Before experimentation, corncob was mixed with catalyst solutions with varying concentrations of sulfuric acid and/or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to allow the catalysts to attach to the materials evenly. LSR is the ratio of the volume of sulfuric acid to the weight of corncob (mL/g). The mixed feedstock was loaded into the reactor. Steam was injected into the reactor from the bottom to heat it until the operating temperature was reached. After a time course of pretreatment, the acetic acid was continuously injected from the bottom by a pump into the reactor. Circulating cold water instantly condensed furfural that was removed from the top of the reactor. All experiments were performed in duplicate under the same

conditions, and their average values were reported (variation < 0.5%).

### Product Analysis

The concentrations of furfural in the liquid were analyzed by gas chromatography (Agilent 6820, Palo Alto, CA, USA) with FID and Innowax polarity column (30 m × 0.32 mm × 0.5 μm). The carrier gas was high purity nitrogen at a flow rate of 1.5 mL/min. The temperature of the detector was 300 °C. The column oven temperature was set to 120 °C for 3 min and 250 °C for 10 min. Samples were syringe-filtered before analysis and analyzed every 10 min. The main fractions of corncobs were cellulose (25.02 ± 1%), hemicelluloses (40.80 ± 1%), and lignin (23.63 ± 1%). The fractions of solid residues were analyzed with the same method. In the theoretical yield, 132 g of hemicellulose can produce 96 g of furfural with complete conversion, as shown by the following scheme:



The furfural yield was calculated according to the following equation,

$$Y = \frac{cV}{0.73M} \times 100 \quad (1)$$

where  $Y$  is the yield of furfural (%),  $c$  is the concentration of furfural in the solution (g/L),  $V$  is the volume of furfural solution (L), and  $M$  is the weight of hemicellulose in the corncob (g).

The side products in the liquid were analyzed by GC-MAS (Clarus 500) and Agilent J&W GC columns (30 m × 0.32 mm × 0.23 μm). The carrier gas was high purity nitrogen at a flow rate of 1 mL/min. The temperature of the detector was 250 °C. The column oven temperature was set to 40 °C for 5 min and 250 °C for 5 min. Samples were syringe-filtered before analysis and analyzed every 10 min.

## RESULTS AND DISCUSSION

### Co-Catalysis of Sulfuric Acid and Acetic Acid

#### *Impact of acetic acid*

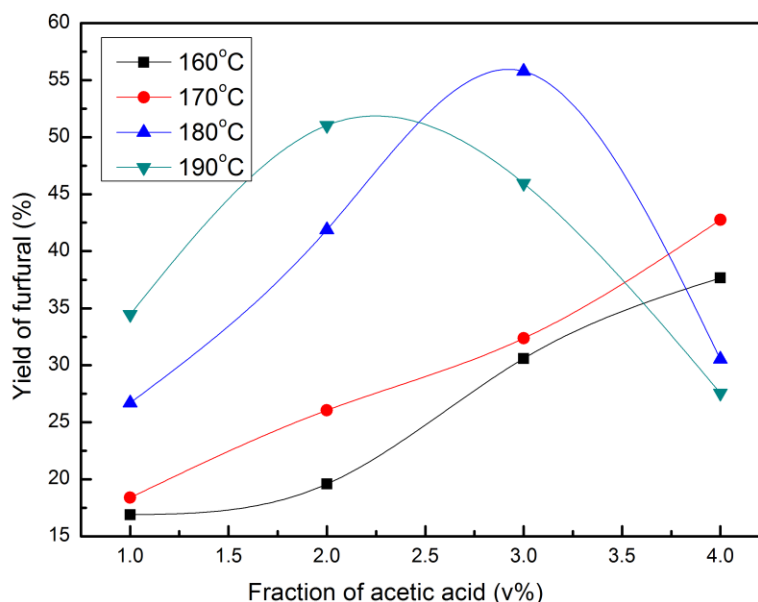
Acetic acid, a byproduct of hemicellulose hydrolysis into pentose, also played the role of catalyst for furfural production from biomass, which is called autocatalysis. Sánchez *et al.* (2013) investigated the final degradation compounds for the furfural production from biomass, and the results showed that acetic acid was the most abundant final degradation compound with up to 5.23 ± 0.21 g/L using 2% (v/v) HCl as a catalyst. Therefore, acetic acid as a byproduct can be separated from the furfural distillation process and returned to the hydrolysis reactor as a catalyst for furfural production.

The catalytic impact of acetic acid on furfural production was evaluated with the concentration of acetic acid ranging from 3 v% to 9 v% at varying temperatures of 160 °C to 190 °C. The results are shown in Fig. 2.

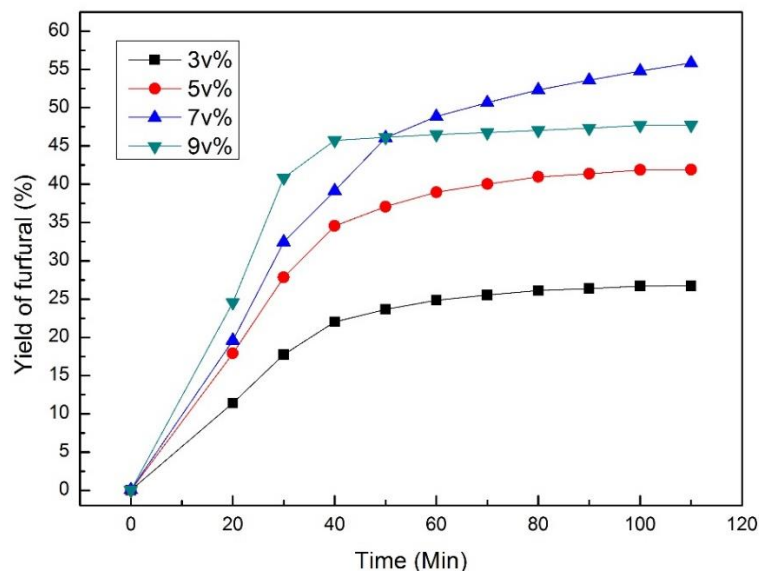
At a relatively lower temperature of 160 °C and 170 °C, the furfural yield increased with the concentration of acetic acid from 3 v% to 9 v%. At 180 °C, a furfural yield of 55.78% was obtained when the concentration of acetic acid was 7 v%. With a further increase in acetic acid from 7 v% to 9 v%, the furfural yield decreased sharply from 55.78% to 46.00% (Fig. 3), which also occurred at 190 °C. The gradual decrease in furfural yield indicated that the rate of furfural loss to decomposition products becomes higher than that of furfural production.

Higher temperatures and higher concentration of acetic acid could favor the hydrolysis of hemicellulose to xylose and the dehydration of xylose to furfural. It also could accelerate many side reactions, such as condensation of furfural with intermediates, degradation of furfural, esterification of cellulose with acetic acid, and the polymerization of furfural with lignin (Guenic *et al.* 2015).

The hemicellulose hydrolysis to xylose and xylose dehydration to furfural are both hydrogen ion-catalyzed reactions, and the reaction rates depend on the acid concentration. Chen *et al.* (2015) studied the kinetics of xylose dehydration into furfural, furfural degradation, and condensation using acetic acid as a catalyst. The results showed that the acetic acid concentration index was 0.1676 for xylose dehydration, 0.1375 for furfural degradation, and 0.1676 for furfural condensation. Figures 2 and 3 indicated that to achieve high furfural yield, the concentration of acetic acid should be as high as 7 v%. Therefore, to decrease acetic acid consumption, the co-catalytic effects of sulfuric acid and acetic acid on furfural yield were investigated.



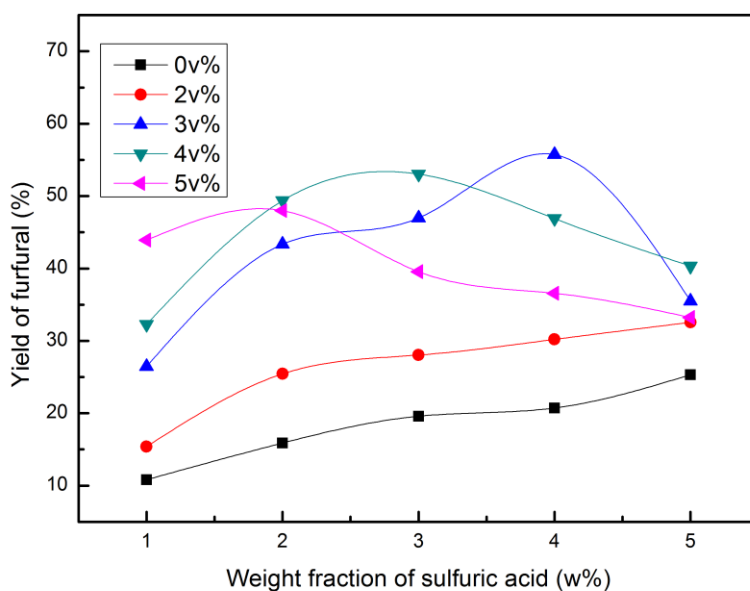
**Fig. 2.** Influence of acetic acid from 3 v% to 9 v% and reaction temperature on furfural yield. The conditions were 100 g of corncob with a pretreatment time of 10 min.



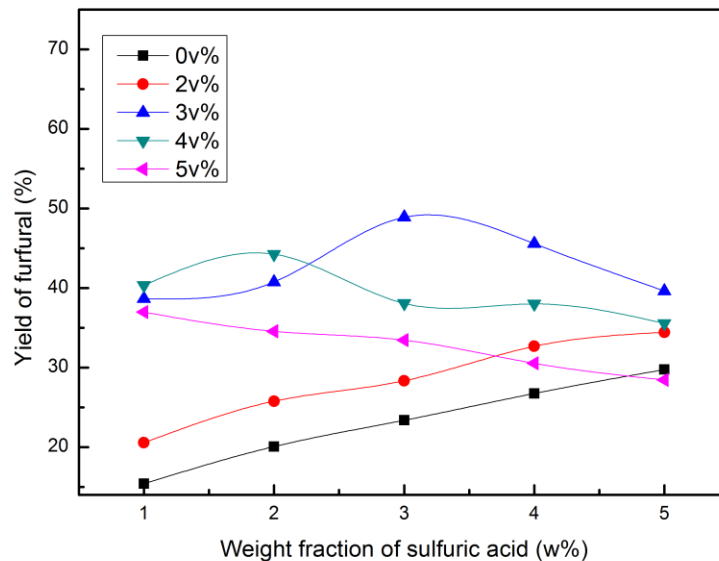
**Fig. 3.** The influence of acetic acid and reaction time on furfural yields. The conditions were 100 g of corncob with a pretreatment time of 10 min.

#### *Impact of sulfuric acid*

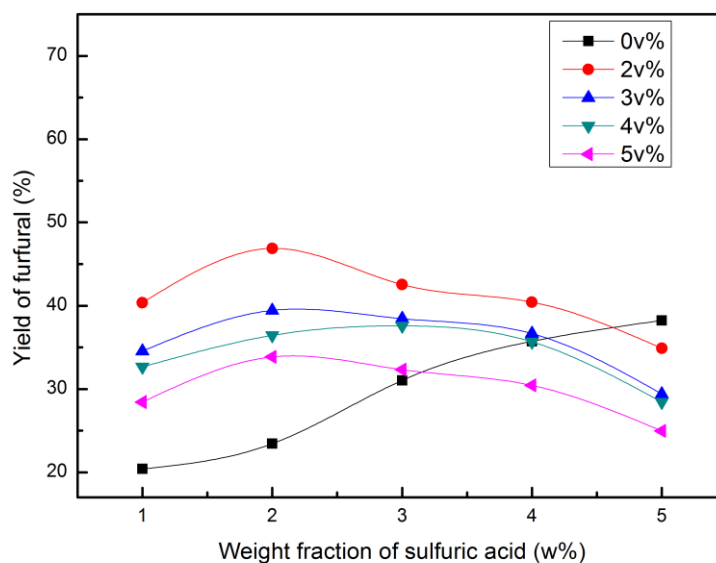
The co-catalytic effects of sulfuric acid and acetic acid on furfural yield are shown in Fig. 4. The maximum furfural yield was 55.85% with 4 wt.% sulfuric acid, LRS of 0.6 mL/g, and 3 v% acetic acid, which was almost the same level as compared with the results of 7 v% acetic acid alone (Fig. 3). The amount of acetic acid decreased from 7 v% to 3 v% using LRS of 0.6 mL/g with 4 wt.% sulfuric acid.



a



b



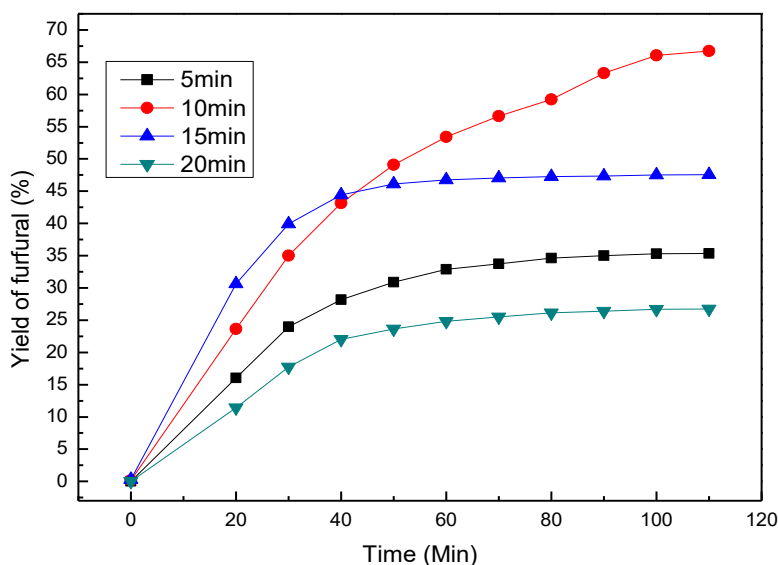
c

**Fig. 4.** The co-catalytic effect of sulfuric acid (1 wt.% - 5 wt.%,) and acetic acid (0 v% - 5 v%) on furfural yield. a: LSR = 0.6 g/mL; b: LSR = 1.0 g/mL; c: LSR = 1.5 g/mL

Compared with the work of Bamufleh *et al.* (2013) using 15 wt.% H<sub>2</sub>SO<sub>4</sub> and 50 mL/g LSR at 140 °C for furfural production, the acid consumption was dramatically decreased with the use of the co-catalysts sulfuric acid and acetic acid. Furthermore, the adverse effects of sulfuric acid, such as the corrosion of steel and safety problems, could be avoided (Mehdi and Pedram 2012). Also, the separation, purification, and recovery of acids would be less challenging because recycling acetic acid is easier than that of sulfuric acid (Vanderghem *et al.* 2012).

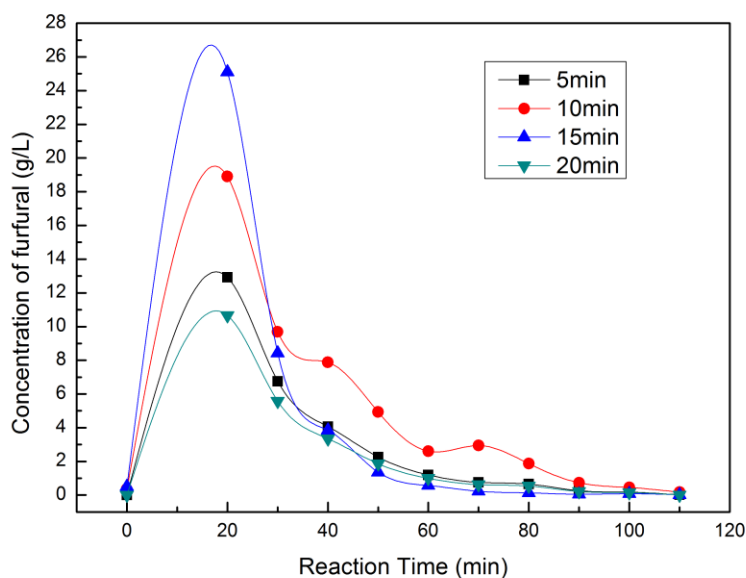
As shown in Fig. 4, the yield of furfural decreased from 55.74% to 36.67% at 3 v% CH<sub>3</sub>COOH, 4 w% H<sub>2</sub>SO<sub>4</sub> when the LSR increased from 0.6 to 1.5. In Fig. 4a, the yield of furfural increased from 26.48% to 55.74% with sulfuric acid from 1 w% to 4 w%, then the yield decreased to 35.50% when sulfuric acid was 5w% at 3v% CH<sub>3</sub>COOH. With the LRS or weight fraction of sulfuric acid increasing, the amount of H<sup>+</sup> increased. A high concentration of acid could accelerate many side reactions, such as condensation of furfural with intermediates, self-resinification of furfural, and the polymerization of furfural with lignin. Moreover, with an increase of LSR, more water was mixed with corncob, and interstitial water hindered homogeneous steam distribution into the granular corncob (Bamufleh *et al.* 2012). So the level of LSR was chosen as 0.6, which is slightly below saturated water content, making it convenient to absorb acetic acid in the steam.

In this study, sulfuric acid was mixed with biomass before experiments, and furfural was removed after a time course of pretreatment. The effect of time courses (5 to 20 min) of pretreatment on furfural production was investigated at 180 °C (Fig. 5). The furfural yield was 35.33% at the time course of 5 min and 66.74% at 10 min; it decreased from 47.53% to 26.72% from 15 min to 20 min. After 20 min, the furfural concentrations under different pretreatment times all reached their peak values and then decreased dramatically (Fig. 6). The furfural yield was strongly dependent on the duration of pretreatment. During this time course, H<sup>+</sup> diffused into the solid matrix and combined with the oxygen of glycosidic bonds. The bond ruptured, forming oligomeric sugar or monosaccharide. The reaction products diffused into the liquid phase, and xylose dehydrated to furfural (Weingarten *et al.* 2010). With longer pretreatment time course, the resulting furfural could not be removed immediately from the reactor, which caused several side reactions to occur. These included the decomposition of furfural into formic acid and the condensations of furfural with furfural, xylose, and lignin-related phenolic compounds (Brazdausks *et al.* 2016). The key to avoiding these side reactions and controlling the furfural recovery and furfural loss was to shorten the residence time of furfural in the aqueous phase (Mao *et al.* 2012).



**Fig. 5.** The effect of pretreatment time on furfural yield. The conditions were 100 g corncob, 5 g FeCl<sub>3</sub>·6H<sub>2</sub>O, 4 wt.% H<sub>2</sub>SO<sub>4</sub> with LSR = 0.6 mL/g, and 3 v% of acetic acid at 180 °C





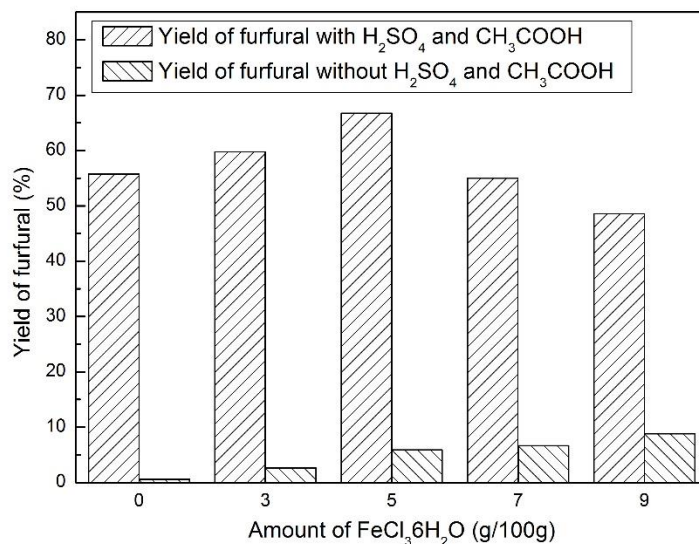
**Fig. 6.** The effect of pretreatment time on furfural concentration. The conditions were 100 g corncob, 5 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 4 wt.%  $\text{H}_2\text{SO}_4$  with LSR = 0.6 mL/g, and 3 v% of acetic acid at 180 °C.

In the pretreatment process, sulfuric acid had a better catalytic effect because  $\text{H}_2\text{SO}_4$  is a strong acid and was not easily evaporated, which made both depolymerization and dehydration occur simultaneously (Jensen *et al.* 2008).

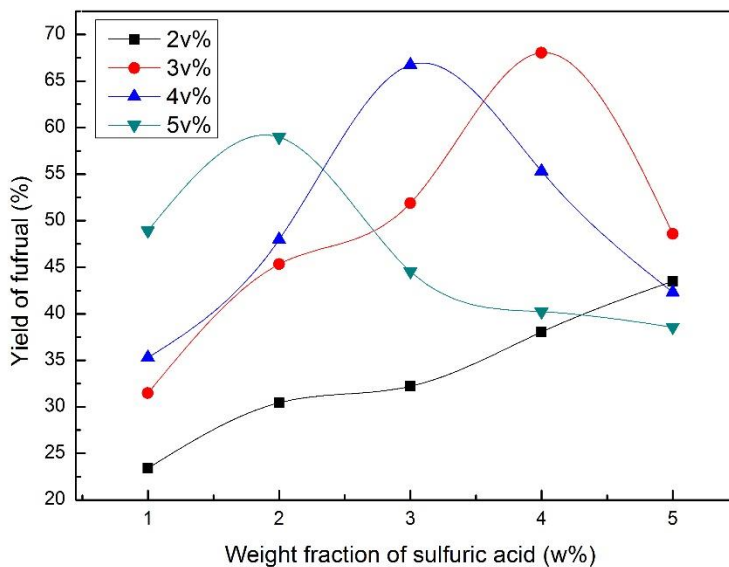
### Furfural Production with the Assistance of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

On the basis of experimental results and literature reports, chloride ions can enhance furfural formation from D-xylose in dilute aqueous acidic solutions (Liu *et al.* 2006; Mao *et al.* 2008, 2013; Xu 2016).  $\text{Fe}^{3+}$  has a relevant catalytic effect on the reaction of xylose (Zhi *et al.* 2015). Furthermore, the reaction of xylose catalyzed by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is much faster than reactions with other chlorine salts (Marcotullio and De 2010). To determine the effect of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  on the yield of furfural, the amounts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  without acid and the amounts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with 4 wt.% sulfuric acid LSR of 0.6 mL/g and 3 v% acetic acid at 180 °C were investigated. Figure 7 shows that the yield of furfural just in the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  without any sulfuric acid or acetic acid increased with the amount  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . But the maximum yield of furfural was just only 8.82%. However, with the acid, the furfural yield could reach 68.04%. These findings showed that the effect of co-catalyst of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with acid is better than the effect of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  without acid. Figure 7 also showed with the acid that the furfural yield increased from 55.85% to 68.04% with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  increasing from 0 g to 5 g, respectively.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  showed remarkable reactivity and considerably accelerated the reaction.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  displayed a superior performance on the hydrolysis of lignocellulosic biomass (Marcotullio and De 2010). When the amount of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was increased to 7 g, the furfural yield decreased to 54.98%. Thus, increasing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  concentrations favored furfural formation, but excessive  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  caused more furfural degradation.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  not only catalyzed furfural formation but accelerated furfural degradation and condensation (Zhang *et al.* 2014 b).

The influence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  on furfural yield was evaluated in the M-O-L acid catalyzed process. The catalytic effects of M-O-L acid [sulfuric acid (1 wt.% to 4 wt.%), acetic acid (2 v% to 5 v%) with 5 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ], and 100 g corncobs with 10 min pretreatment time at 180 °C were investigated.



**Fig. 7.** Influence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  on furfural yield. The conditions were 100 g corncobs, with 4 wt.% sulfuric acid of LSR = 0.6 g/mL, 3v% acetic acid and without acid, 180 °C, and a pretreatment time of 10 min.

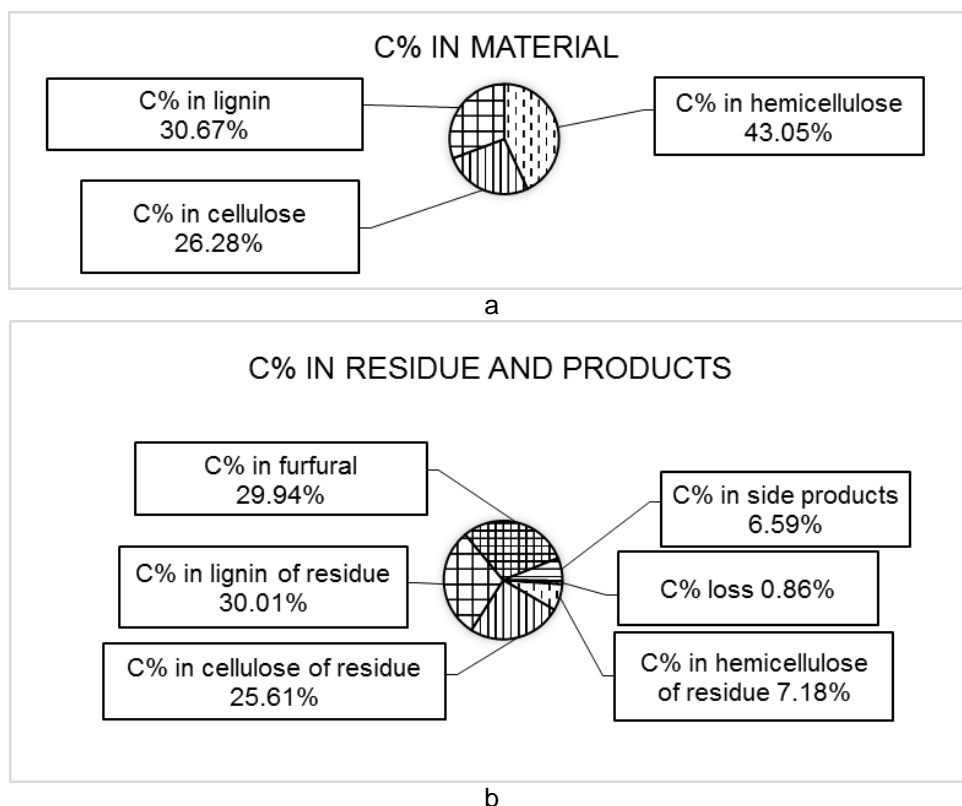


**Fig. 8.** The co-effect of sulfuric acid, acetic acid, and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  on the yield of furfural. The conditions were 100 g corncobs, LSR = 0.6, 5 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 180°C, and a pretreatment time of 10 min.

Figure 8 shows that the yield of furfural had a similar trend as in Fig. 4, but the yield apparently increased because of the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The maximum furfural yield was 55.85% at 4 wt.% sulfuric acid and 3 v% acetic acid without  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . When comparing a 20.74% furfural yield at just 4 wt.% sulfuric acid and a 26.7% yield of furfural at 3 v% acetic acid, the co-catalytic effect of sulfuric acid and acetic acid was evident. The furfural yield reached 68.04% with the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Fig. 8).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  may significantly increase hemicellulose degradation with high xylose recovery and low cellulose removal compared with other chlorides (Liu *et al.* 2006, 2009). Metal ions ( $\text{Fe}^{3+}$ ) penetrate and damage the fiber structures in biomass, making it easier to liberate acetylated or formylated xylose oligomers (Guenic *et al.* 2015). Metal chlorides also promote the isomerization of xylose to xylulose, which is easier to dehydrate into furfural (Marcotullio and De 2010; Kim *et al.* 2012). The furfural yields initially increased with a fraction of acetic acid from 2 v% to 4 v%, then decreased when the fraction of acetic acid was 5 v%. If the amount of acid exceeded the optimum value, the side-reaction was also accelerated.

### Mechanism of Furfural Production Process by M-O-L Acid Catalyzed

The generation of furfural from lignocellulosic biomass is a complex process involving the decomposition of hemicellulose to oligomeric sugars, the hydrolysis of oligomeric sugars to pentose, the dehydration of pentose to furfural, furfural condensation reactions, and degradation leading to furfural consumption. The mechanism of furfural production by M-O-L acid catalyzed process is shown in Fig. 9.



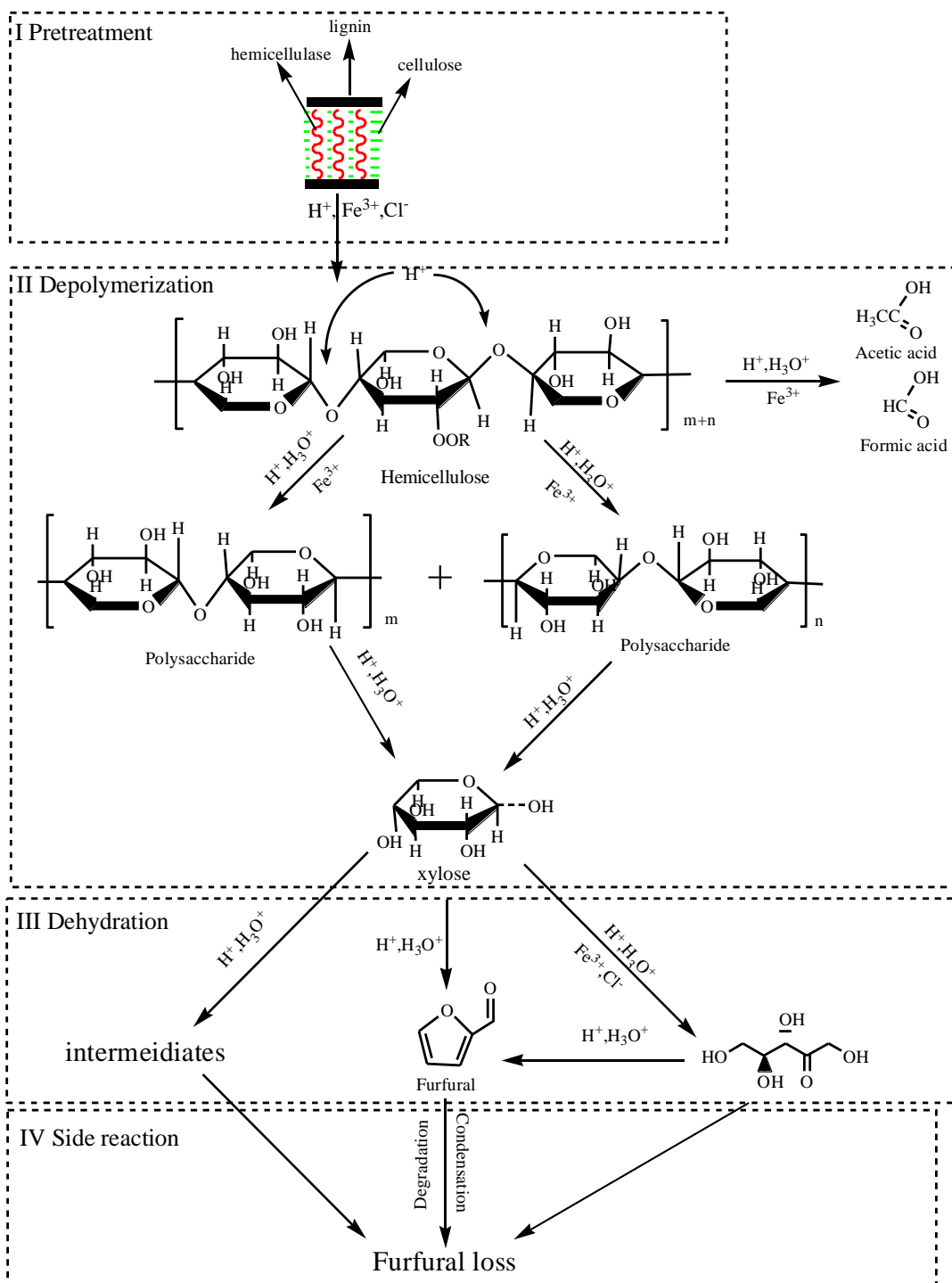
**Fig. 9.** The content of C% in the component basing on the material and the best reaction condition. a: C% in material, b: C% in residue and products

In the pretreatment step, material was mixed with sulfuric acid and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in order to adhere catalysts to materials evenly and achieve the best reaction.

At the depolymerization stage,  $H^+$  and  $Fe^{3+}$  played important roles.  $H^+$  was provided by sulfuric acid and acetic acid. When using 4 wt% 60 mL sulfuric acid, the amount of acetic acid decreased from 7v% to 3v% to reach almost the same furfural yield 55.78%. The co-catalyst effect of sulfuric acid and acetic acid decreased the total amount of acid. Under the action of  $H^+$ , the long chain of hemicellulose contained in lignocellulosic biomass is hydrolyzed at high temperatures to xylose and other monosaccharides (Kumar *et al.* 2015). And from the Fig. 9, the C% levels in cellulose and in lignin of material were 26.28% and 30.67% respectively, whereas after the reaction, the C% in cellulose and in lignin were 25.61% and 30.01%, respectively. Based on these numbers, it could be inferred that the cellulose loss ratio was 2.52%, and the lignin loss ratio was 2.08%. This means that the cellulose and lignin fractions remained almost unreacted under the reaction condition in these experiments. Moreover, with adding 5g  $FeCl_3 \cdot 6H_2O$ , the yield of furfural increased from 55.85% to 68.04%.  $Fe^{3+}$  penetrates and damages the fiber structures in biomass, making it much easier to liberate acetylated or formylated xylose oligomers (Yu *et al.* 2011). In the process of hemicellulose hydrolysis into pentose catalyzed by  $Fe^{3+}$  and  $H^+$ , acetic acid and formic acid are produced as byproducts

At the dehydration stage,  $FeCl_3 \cdot 6H_2O$  affected the yield of furfural, as in the case of the depolymerization stage. But when just using  $FeCl_3 \cdot 6H_2O$  without acid as the catalyst the yield of furfural was only 8.82%, but the yield of furfural could reach 68.04% with acid. As shown in Fig. 10,  $Fe^{3+}$  and  $Cl^-$  could promote isomerization of xylose to form xylulose. However, hemicellulose hydrolysis to xylose and xylose dehydration to furfural are both hydrogen ion catalyzed reactions. That means that the effect of co-catalyst of  $FeCl_3 \cdot 6H_2O$  with acid is better than the effect of  $FeCl_3 \cdot 6H_2O$  without acid.

Excessive acid, metal chlorides, long pretreatment time, and high temperatures cause condensation and degradation, which lead to furfural loss, which has been detected by GC-MS in the products as shown in the Table 1. When acetic acid was increased from 7v% to 9v%, the yield of furfural decreased sharply from 55.78% to 46.00%. If the amount of  $FeCl_3 \cdot 6H_2O$  was increased from 5 g to 7 g, the yield of furfural was reduced from 68.04% to 54.98%. High acetic acid concentrations and high  $FeCl_3 \cdot 6H_2O$  concentrations caused much stronger side reactions between furfural, cellulose, lignin, and glucose, including the condensation of furfural with intermediates and the degradation of furfural (Lam *et al.* 2009). The proper amount in our experiment is 3v% acetic acid, 60 mL of 4.0wt.% sulfuric acid and 5 g  $FeCl_3 \cdot 6H_2O$  per 100 g of biomass. At the temperature of 160 °C and 170 °C, the yield of furfural increased with concentration of acetic acid. At relatively low temperature, the furfural yield and reaction rate both increased with increasing  $H^+$  ion concentration at elevated temperatures. At 180 °C, the highest yield of furfural was 55.78% when the concentration of acetic acid was 7 v%. At 190 °C, the highest yield of furfural was 51.04% at 5 v% acetic acid concentration. Higher hydrolysis temperature favors both a higher furfural yield and faster formation, but the rate of furfural loss is much faster than its rate of formation at the maximum concentration, which causes further furfural loss (Hisham *et al.* 2012). From the previous experiments, the 180 °C was the proper reaction temperature. The furfural yield was 35.33% at the time course of 5 min and 66.74% at 10 min; it decreased from 47.53% to 26.72% from 15 min to 20 min. With long pretreatment time over 15min, the furfural in the viscous aqueous phase facilitates more side reactions such as the esterification of cellulose with acetic acid and the polymerization of furfural with lignin.



**Fig. 10.** The mechanism of furfural production by M-O-L acid integrated process

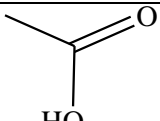
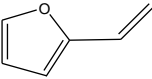
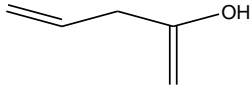
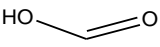
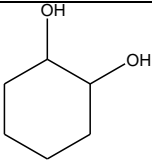
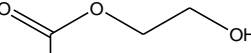
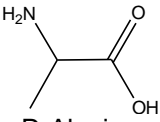
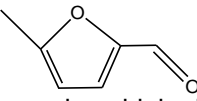
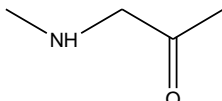
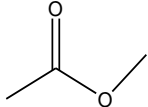
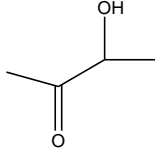
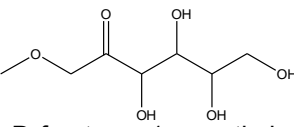
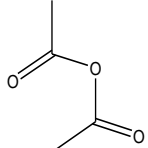
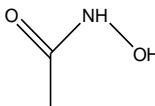
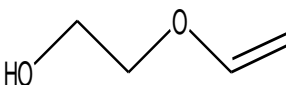
I Pretreatment: Corn cobs are mixed with varying concentrations of sulfuric acid and/or  $FeCl_3 \cdot 6H_2O$  before experimentation to make catalysts attach to materials evenly.

II Depolymerization:  $H^+$  provided by sulfuric acid and acetic acid hydrolyzed the long chain of hemicellulose to form xylose and other monosaccharides at high temperatures. With the effect of  $H^+$  and  $Fe^{3+}$ , acetic acid and formic acid were produced.

III Dehydration: Xylose was isomerized to form xylulose, which was easier to dehydrate into furfural.  $H^+$ ,  $Fe^{3+}$ , and  $Cl^-$  catalyzed the subsequent dehydration steps to produce furfural.  $H_3O^+$  and  $H^+$  also catalyzed xylose to form other intermediates.

IV Side reaction: Including condensation and degradation caused the furfural loss.

**Table 1.** The Composition of Side Products

 <p>HO Acetic acid. C<sub>2</sub>H<sub>4</sub>O<sub>2</sub></p>	 <p>Vinylfuran C<sub>6</sub>H<sub>6</sub>O</p>	 <p>4-penten-2-ol C<sub>5</sub>H<sub>8</sub>O</p>
 <p>formic acid CHO<sub>2</sub></p>	 <p>Cis-1,2-cyclohexanediol C<sub>6</sub>H<sub>12</sub>O<sub>2</sub></p>	 <p>1,2-ethanediol,onoacetate C<sub>4</sub>H<sub>8</sub>O<sub>3</sub></p>
 <p>D-Alanine C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>N</p>	 <p>2-furancarboxaldehyde, 5-methyl- C<sub>6</sub>H<sub>6</sub>O<sub>2</sub></p>	 <p>N-methylglycine C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>N</p>
 <p>Acetic acid methyl ester C<sub>3</sub>H<sub>6</sub>O<sub>2</sub></p>	 <p>2-butanone,3-hydroxy- C<sub>4</sub>H<sub>8</sub>O<sub>2</sub></p>	 <p>D-fructose, 1-o-methyl- C<sub>7</sub>H<sub>13</sub>O<sub>6</sub></p>
 <p>Acetic anhydride C<sub>4</sub>H<sub>6</sub>O<sub>3</sub></p>	 <p>Acetohydroxamic acid C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N</p>	 <p>Ethanol,2-(vinyloxy)- C<sub>4</sub>H<sub>8</sub>O<sub>2</sub></p>

## CONCLUSIONS

1. With the co-catalytic effects of sulfuric acid and acetic acid, the drawbacks caused by the high concentration of sulfuric acid such as the corrosion of steel and safety problems could be avoided. The maximum furfural yield was 55.85% with 4wt.% sulfuric acid and 3v% acetic acid, which was almost the same level compared with the results of 7v% acetic acid alone. The amount of acid was decreased by co-catalyst of sulfuric acid and acetic acid.
2. Metal chlorides could lead to a remarkable improvement in the reaction rate of xylose conversion, and they have been inferred to induce an alternative mechanism for xylose dehydration into furfural via the formation of xylulose, which is easier to dehydrate into furfural. The yield of furfural was strongly increased from 55.85% to 68.04% by using FeCl<sub>3</sub>·6H<sub>2</sub>O. By contrast, when but using only FeCl<sub>3</sub>·6H<sub>2</sub>O without acid, the

yield of furfural was just 8.82% because hemicellulose hydrolysis to xylose and xylose dehydration to furfural mainly depend on the hydrogen ion.

3. A M-O-L acid catalyzed process for furfural production from corncob was proposed, in which each component of the catalytic system plays its respective role. With the process of M-O-L acid (mineral acid, organic acid and Lewis acid) catalyzing, a maximum furfural yield of 68.04% was obtained at 4.0 wt.% H<sub>2</sub>SO<sub>4</sub> of 60 mL, 3 v% acetic acid, and 5 g FeCl<sub>3</sub>·6H<sub>2</sub>O per 100 g biomass.

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## REFERENCES CITED

- Abad, S., Santos, V., and Paraj, J. C. (1997). "Furfural from wood in catalyzed acetic acid media: A mathematical assessment," *Bioresource Technol.* 62, 115-122. DOI: 10.1016/S0960-8524(97)00076-X
- Agirrezabal -Telleria, I., Requies, J., Güemez, M. B., and Arias, P. L. (2014). "Dehydration of d-xylose to furfural using selective and hydrothermally stable arenesulfonic SBA-15 catalysts," *Appl. Catal. B-Environ.* 145, 34-42. DOI: 10.1016/j.apcatb.2012.11.010
- Avci, A., Saha, B. C., Kennedy, G. J., and Cotta, M. A. (2013). "High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production," *Ind. Crop Prod.* 50, 478-484. DOI: 10.1016/j.indcrop.2013.07.055
- Bamufleh, H. S., Alhamed, Y. A., and Daous, M. A. (2013). "Furfural from midribs of date-palm trees by sulfuric acid hydrolysis," *Ind. Crop Prod.* 42, 421-428. DOI: 10.1016/j.indcrop.2012.06.008
- Brazdausks, P., Paze, A., Rizhikovs, J., Puke, M., Meile, K., Vedernikovs, N., Tupciauskas, R., and Andzs, M. (2016). "Effect of aluminium sulphate-catalysed hydrolysis process on furfural yield and cellulose degradation of *Cannabis sativa* L. shives," *Biomass Bioenerg.* 89, 98-104. DOI: 10.1016/j.biombioe.2016.01.016
- Bruce, S. M., Zong, Z., Chatzidimitriou, A., Avci, L. E., Bond, J. Q., Carreon, M. A., and Wettstein, S. G. (2016). "Small pore zeolite catalysts for furfural synthesis from xylose and switchgrass in a  $\gamma$ -valerolactone/water solvent," *J. Mol. Catal. A-Chem* 9791, 1-5. DOI: 10.1016/j.molcata.2016.02.025
- Chen, Z., Zhang, W., Xu, J., and Li, P. (2015). "Kinetics of xylose dehydration into furfural in acetic acid," *Chin. J. Chem. Eng.* 23(4), 659-666. DOI: 10.1016/j.cjche.2013.08.003
- Choudhary, V., Sandler, S. I., and Vlachos, D. G. (2012). "Conversion of xylose to furfural using Lewis and Brønsted acid catalysts in aqueous media," *ACS Catal.* 2(9), 2022-2028. DOI: 10.1021/cs300265d
- Guenic, S. L., Delbecq, F., Ceballos, C., and Len, C. (2015). "Microwave-assisted

- dehydration of D-xylose into furfural by diluted inexpensive inorganic salts solution in a biphasic system,” *J. Mol. Catal. A-Chem* 410, 1-7. DOI: 10.1016/j.molcata.2015.08.019
- Herrera, A., Téllez-Luis, S. J., González-Cabriales, J. J., and Ramírez, J. A. (2004). “Effect of the hydrochloric acid concentration on the hydrolysis of sorghum straw at atmospheric pressure,” *J. Food Eng.* 63(1), 103-109. DOI: 10.1016/S0260-8774(03)00288-7
- Jensen, J., Morinelly, J., Aglan, A., Mix, A., and Shonnard, D. R. (2008). “Kinetic characterization of biomass dilute sulfuric acid hydrolysis: Mixtures of hardwoods, softwood, and switchgrass,” *AIChE Journal* 54(6), 1637-1645. DOI: 10.1002/aic.11467
- Jing, Q., and Lu, X. (2007). “Kinetics of non-catalyzed decomposition of D-xylose in high temperature liquid water,” *Chin. J. Chem. Eng.* 15(5), 666-669. DOI: 10.1016/S1004-9541(07)60143-8
- Kim, E. S., Liu, S., Abu-Omar, M. M., and Mosier, N. S. (2012). “Selective conversion of biomass hemicellulose to furfural using maleic acid with microwave heating,” *Energ. Fuel* 26(2), 1298-1304. DOI: 10.1021/ef2014106
- Kumar, S., Dheeran, P., Singh, S. P., Mishra, I. M., and Adhikari, D. K. (2015). “Kinetic studies of two-stage sulphuric acid hydrolysis of sugarcane bagasse,” *Renew Energ.* 83, 850-858. DOI: 10.1016/j.renene.2015.05.033
- Lam, P. S., Sokhansanj, S., Jim, L. C., Bi, X. T., and Melin, S. (2009). “Kinetic modeling of pseudolignin formation in steam exploded woody biomass,” in: *8th World Congress of Chemical Engineering*, Montreal, Canada, pp. 23-27. ([https://www.researchgate.net/publication/267679448\\_Kinetic\\_Modeling\\_of\\_Pseudolignin\\_Formation\\_in\\_Steam\\_Exploded\\_Woody\\_Biomass](https://www.researchgate.net/publication/267679448_Kinetic_Modeling_of_Pseudolignin_Formation_in_Steam_Exploded_Woody_Biomass))
- Liu, C. G., and Wyman, C. E. (2006). “The enhancement of xylose monomer and xylotriose degradation by inorganic salts in aqueous solutions at 180 °C,” *Carbohydr. Res.* 341, 2550-2556. DOI: 10.1016/j.carres.2006.07.017
- Liu, L., Sun, J., Li, M., Wang, S., Pei, H., and Zhang, J. (2009). “Enhanced enzymatic hydrolysis and structural features of corn stover by FeCl<sub>3</sub> pretreatment,” *Bioresource Technol.* 100(23), 5853-5858. DOI: 10.1016/j.biortech.2009.06.040
- Mamman, A. S., Lee, J. M., Kim, Y. C., Hwang, I. T., Park, N. J., Hwang, Y. K., Chang, J. S., and Hwang, J. S. (2008). “Furfural: Hemicellulose/xylose-derived biochemical,” *Biofuels Bioprod. Bioref.* 2(5), 438-454. DOI: 10.1002/bbb.95
- Mao, L., Zhang, L., Gao, N., and Li, A. (2012). “FeCl<sub>3</sub> and acetic acid co-catalyzed hydrolysis of corncob for improving furfural production and lignin removal from residue,” *Bioresource Technol.* 123, 324-331. DOI: 10.1016/j.biortech.2012.07.058
- Mao, L., Zhang, L., Gao, N., and Li, A. (2013). “Seawater-based furfural production via corncob hydrolysis catalyzed by FeCl<sub>3</sub> in acetic acid steam,” *Green Chem.* 15(3), 727-737. DOI: 10.1039/C2GC36346A
- Marcotullio, G., and De, J. W. (2010). “Chloride ions enhance furfural formation from d-xylose in dilute aqueous acidic solutions,” *Green Chem.* 12(10), 1739-1746. DOI: 10.1039/B927424C
- Mehdi, D. A. G., and Pedram, F. (2012). “Production of furfural: Overview and challenges,” *Journal of Science & Technology for Forest Products and Processes* 2, 44-53. ([https://www.researchgate.net/publication/261051357\\_PRODUCTION\\_OF\\_FURFURAL\\_OVERVIEW\\_AND\\_CHALLENGES](https://www.researchgate.net/publication/261051357_PRODUCTION_OF_FURFURAL_OVERVIEW_AND_CHALLENGES))



- Oh, S. J., Su, H. J., and Kim, J. S. (2013). "Co-production of furfural and acetic acid from corncob using  $ZnCl_2$  through fast pyrolysis in a fluidized bed reactor," *Bioresource Technol.* 144, 172-178. DOI: 10.1016/j.biortech.2013.06.077
- Park, G., Jeon, W., Ban, C., Woo, H., and Kim, D. (2016). "Direct catalytic conversion of brown seaweed-derived alginic acid to furfural using 12-tungstophosphoric acid catalyst in tetrahydrofuran/water co-solvent," *Energ. Convers. Manage.* 118, 135-141. DOI: 10.1016/j.enconman.2016.03.091
- Peleteiro, S., Santos, V., Garrote, G., and Parajo, J. C. (2016). "Furfural production from eucalyptus wood using an acidic ionic liquid," *Carbohydr. Polym.* 146, 20-25. DOI: 10.1016/j.carbpol.2016.03.049
- Sánchez, C., Serrano, L., Andres, M. A., and Labidi, J. (2013). "Furfural production from corn cobs autohydrolysis liquors by microwave technology," *Ind. Crop Prod.* 42, 513-519. DOI: 10.1016/j.indcrop.2012.06.042
- Vanderghem, C., Brostaux, Y., Jacquet, N., Blecker, C., and Paquot, M. (2012). "Optimization of formic/acetic acid delignification of *Miscanthus × giganteus* for enzymatic hydrolysis using response surface methodology," *Ind. Crop Prod.* 35(1), 280-286. DOI: 10.1016/j.indcrop.2011.07.014
- Weingarten, R., Cho, J., Conner, J. W. C., and Huber, G. W. (2010). "Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating," *Green Chem.* 12(8), 1423-1429. DOI: 10.1039/C003459B
- Xu, W. (2016). *Hydrolysis of Lignocellulosic Biomass to Furfural and Levulinic Acid*, Master's Thesis, East China Univ. of Sci. and Technol., Shanghai, China, pp. 22-35.
- Xu, Z., Li, W., Du, Z., Wu, H., Jameel, H., Chang, H. M., and Ma, L. (2015). "Conversion of corn stalk into furfural using a novel heterogeneous strong acid catalyst in gamma-valerolactone," *Bioresource Technol.* 198, 764-771. DOI: 10.1016/j.biortech.2015.09.104
- Yang, W., Li, P., Bo, D., and Chang, H. (2012). "The optimization of formic acid hydrolysis of xylose in furfural production," *Carbohydr. Res.* 357, 53-61. DOI: 10.1016/j.carres.2012.05.020
- Yu, Q., Zhuang, X., Yuan, Z., Qi, W., Wang, Q., and Tan, X. (2011). "The effect of metal salts on the decomposition of sweet sorghum bagasse in flow-through liquid hot water," *Bioresource Technol.* 102(3), 3445-3450. DOI: 10.1016/j.biortech.2010.10.084
- Zhang, L., Yu, H., Wang, P., and Li, Y. (2014). "Production of furfural from xylose, xylan and corncob in gamma-valerolactone using  $FeCl_3 \cdot 6H_2O$  as catalyst," *Bioresource Technol.* 151, 355-360. DOI: 10.1016/j.biortech.2013.10.099
- Zhi, Z., Li, N., Qiao, Y., Zheng, X., Wang, H., and Lu, X. (2015). "Kinetic study of levulinic acid production from corn stalk at relatively high temperature using  $FeCl_3$  as catalyst: A simplified model evaluated," *Ind. Crop Prod.* 76, 672-680. DOI: 10.1016/j.indcrop.2015.07.058

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