



# Catalytic conversion of corncob and corncob pretreatment hydrolysate to furfural in a biphasic system with addition of sodium chloride



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## HIGHLIGHTS

- An efficient biphasic catalytic system was developed for furfural production.
- A highest furfural yield of 81.7% was achieved under optimized conditions.
- 66.1% furfural and 15.9% HMF yields were obtained from raw corncob in this catalytic system.
- The  $\text{SO}_4^{2-}/\text{SnO}_2$ -MMT catalyst displayed good recyclability and stability in this system.

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## ABSTRACT

Catalytic conversion of corncob pretreatment hydrolysate and raw corncob into furfural in a modified biphasic system by  $\text{SO}_4^{2-}/\text{SnO}_2$ -MMT solid catalyst has been developed. The influence of the organic solvent type, organic to water phase ratio, sodium chloride concentration, reaction temperature and time on the furfural production were comparatively evaluated. The results showed that furfural yields of 81.7% and 66.1% were achieved at 190 °C for 15 mins and 190 °C for 20 mins, respectively, for corncob pretreatment hydrolysate and raw corncob by this solid catalyst. The solid catalyst used in this study exhibited good stability and high efficiency applied in the modified biphasic system in addition to excellent recyclability. The proposed catalytic system displayed high performance for catalytic conversion of lignocellulosic biomass into important platform chemicals and has great potential in industrial application.

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## 1. Introduction

The diminishing of fossil fuels and increasing concern about environmental pollution have stimulated the development of sustainable and environmentally-friendly production of fuels and chemicals from renewable resources (Kunkes et al., 2008; Tuck et al., 2012). Lignocellulosic biomass is abundant, cost-effective, and renewable, therefore is considered as an appealing candidate for sustainable substitution of fossil resources (Menon and Rao, 2012). The most prominent examples of lignocellulosic materials include agriculture and forestry residues, industrial or municipal solid wastes, and herbaceous and woody plants. As the largest agricultural country in the world, China has abundant agriculture residues that could be converted to biofuels or bio-based chemicals. In 2010, the total collectable output of agricultural residues was as high as 710.98 million tons, and the total secondary processing

residues was about 144.47 million tons (Ji, 2015). As one of the most important but underused agricultural residues in China, corncob represents a great potential as a raw material for the production of high-value added chemicals, fuels and other industrial products owing to its low lignin content, high hemicelluloses content and energy density (Sahare et al., 2012).

Furfural is one of the most common industrial chemicals that has been considered as important building block for production of biofuels, biochemicals, and biopolymers (Li et al., 2016). The value chains of furanic biofuels are realized by conversion of furfural to different components, such as 2-methylfuran, 2-methyltetrahydrofuran etc. (Dutta et al., 2012). Unfortunately, there is no synthetic route available for furfural production, which is exclusively produced from renewable lignocellulosic resources by hydrolysis and dehydration of xylan that exists in large quantities in hemicelluloses. Consequently, the most applicable furfural production resources are agriculture wastes with high hemicelluloses content, such as corncobs, oat bran, wheat bran etc. Intensive research endeavours have pursued the dehydration of pentose into

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furfural by thermo-chemical processes that were conducted in monophasic, aprotic organic solvents and biphasic systems, employing various types of acid catalysts. To date, several systems using both homogeneous and heterogeneous acid catalysts have been reported, such as mineral acids, inorganic salts, metal oxides, solid acids, as well as ionic liquids (Serrano-Ruiz et al., 2012). Among them, furfural production from hemicelluloses-derived xylose by mineral acids, such as sulfuric, phosphoric, metal salt or hydrochloric acid, is a reasonably mature technology. However, the reaction media is corrosive, difficult to be recovered, and pose environmental and health risks, and more important, current yields of furfural in these systems are relatively low (<60%) (Karinen et al., 2011). On the other hand, solid acid catalysts have been implemented in the furfural production process in recent years, considering the environmental and economical issues (Bhaumik and Dhepe, 2014; Li et al., 2014). Widely reported solid acid catalysts, including zeolites, acid-functionalized MCM materials, heteropoly acids, sulfated zirconia, exfoliated titanate, niobate, and so on (Dias et al., 2005, 2006; Lima et al., 2008; Zhang et al., 2012), exhibited superior furfural production performances than homogeneous catalyst and were easier to be recovered, thus offering opportunities to explore more valuable downstream products for the furfural industry. However, most of these catalysts underwent morphological changes during the reactions (Sahu and Dhepe, 2012) and prone to inactivate after use. Therefore, synthesis of solid acid catalyst with good thermal and chemical stabilities in various reaction systems besides improving the furfural yields is essential to make the overall process attractive and feasible.

The reaction system is another key issue that involves in the furfural production process. Undoubtedly, water is the most inexpensive and eco-friendly solvent that has been maturely employed in furfural production industry. But as a polar protic solvent, the furfural yield in a pure water system is usually constricted due to the limitation of furfural solubility (Mellmer et al., 2014). Therefore, intensive studies have been focused on various biphasic systems that composed by water and an organic solvent, with or without addition of cosolvents. The choice of the organic phase is extremely vital because the simultaneous extraction of furfural into this organic solvent phase has been proved to be beneficial to furfural yields by preventing its rapid degradation to chars and humins under high reaction temperature (Zhang et al., 2013). The organic phases often reported in furfural production biphasic system are toluene, methyl isobutyl ketone (MIBK), dimethyl sulfoxide (DMSO), 2-butanol and n-butanol (Pholjaroen et al., 2013). Wang et al. reported a maximum furfural yield of 63% by catalytic conversion of xylose at 130 °C for 6 h in the water/DMSO system (Wang et al., 2014). In addition, biomass-derived Gamma-valerolactone (GVL) as a monophasic solvent shows significant improvement compared to the conversion of xylose in water (Xu et al., 2015), with a high furfural yield of 60.6% achieved from corn stalk in 100 min at 200 °C reported (Zhang et al., 2016).

In this paper, we report on a feasible biphasic system that employs toluene as the extracting layer to improve the furfural yield from pre-hydrolyzed corncob liquor and raw corncob by a  $\text{SO}_4^{2-}/\text{SnO}_2$  MMT solid catalyst. Commonly used organic solvents were firstly screened and the impact of NaCl as a phase modifier was determined to achieve a high furfural yield and conversion selectivity. In addition, the volume ratio of the toluene to water phase, reaction temperature, reaction duration were evaluated by using corncob hydrolysate and raw corncob as reactants. The solid catalyst  $\text{SO}_4^{2-}/\text{SnO}_2$  MMT employed in this study was proved to have a good recyclability and was characterized before and after use by Element Analysis (EA), Brunauer–Emmett–Teller (BET) method, Scanning Electron Microscopy (SEM), and Pyridine-adsorbed Fourier Transform Infrared Spectroscopy (PA-FTIR).

## 2. Methods

### 2.1. Materials

Corncoobs obtained from farms in Xinxiang (Henan Province, P. R. China) was washed and dried at 90 °C to constant weight, and then milled into a particle size of 40–60 mesh for future use. The chemical compositions of corncoobs were determined following the National Renewable Energy Laboratory (NREL) analytical procedure (LAP) (Sluiter et al., 2008), which were 32.63% of cellulose, 31.7% of hemicellulose, 16.9% of lignin, and 2.1% of ash. Oxalic acid, sodium chloride, and other chemical reagents were all purchased from Sinopharm Group Chemical Reagent Co. Ltd. (Shanghai, P. R. China). Organic solvents, including toluene, methyl isobutyl ketone (MIBK), cyclopentyl methyl ether (CPME), valerolactone (GVL) were purchased from Changzhou Runyou Commercial and Trading Co. Ltd. (Changzhou, P. R. China).

### 2.2. Catalytic conversion of xylose-rich solution to furfural

The xylose rich solution was obtained from oxalic acid pretreatment of corncob as described in previous publication (Qing et al., 2015), with a xylose concentration determined as 20 mg/mL. The xylose-rich liquor was mixed with organic solvents in a certain ratio with the addition of different amounts of solid acid catalyst in a sealed stainless steel reactor. Then the reactor was rapidly heated to the target temperature by a porcelain heating jacket and hold for different reaction durations. After the reaction, the reactor was cooled down to room temperature in an iced water bath, and the products and remaining reactants in both organic and water phases were filtrated with 0.22 μm filter membranes before quantification.

### 2.3. Preparation of the $\text{SO}_4^{2-}/\text{SnO}_2$ MMT solid catalyst

0.7 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and 2.1 g montmorillonite (weight ratio = 1:3) were mixed and dissolved in 50 mL ethanol solution. After intense agitation under room temperature and atmospheric pressure, a homogeneous turbid liquid formed, which was adjusted to pH 6.0 by concentrated ammonium hydroxide. Then the MMT- $\text{Sn}(\text{OH})_4$  colloidal solution was oven-dried at 70 °C for 12 h, then kept under 90 °C for 12 h to dry off. Finally 2 g of this solid was soaked in 30 mL 1.0 mol/L  $\text{H}_2\text{SO}_4$  for 3 h, then filtrated and oven-dried at 110 °C for 3 h and baked at 500 °C for another 3.5 h.

### 2.4. Product analysis

The concentration of xylose, glucose, furfural, and HMF in water phase were quantified by a Waters Alliance High Performance Liquid Chromatography (HPLC, Model 2695, Waters Corporation, Milford, MA) with external standard method, equipped with an Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA) and a refractive index detector (Waters 2414). The temperature of column oven was maintained at 65 °C and 5 mM sulfuric acid was used as the mobile phase with a flow rate of 0.6 mL/min. Furfural in the organic phase was determined by a gas chromatograph-mass spectrometer (GC-MS, Agilent 7890/5975), with nitrogen as the carrier gas. The injection and detector ports were maintained at 300 °C, while the column temperature was maintained initially at 80 °C for 3 min and then heated to 280 °C with a heating rate of 15 °C/min. Furfural yield, xylose conversion, furfural selectivity, HMF yield, and levulinic acid yield were calculated based on following equations:

$$\text{Furfural yield}(\%) = \frac{\text{Furfural produced (g)}}{\text{Original xylose in hydrolysate (g)}} \times \frac{150}{96} \times 100$$

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