



Catalytic hydrothermal pretreatment of corncob into xylose and furfural via solid acid catalyst



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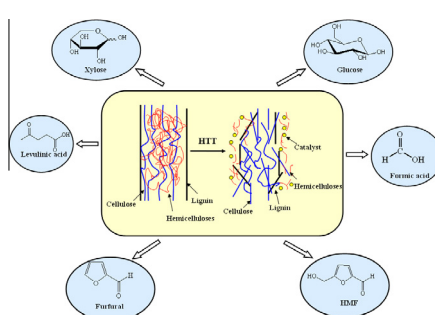
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HIGHLIGHTS

- Selectively catalytic hydrothermal pretreatment of corncob was investigated.
- Solid acid ($\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2/\text{La}^{3+}$) was as a catalyst.
- Xylose and furfural were the main hydrolysates.
- Highest furfural yield (6.18 g/100 g) with 6.80 g/100 g xylose yield was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Selectively catalytic hydrothermal pretreatment of corncob into xylose and furfural has been developed in this work using solid acid catalyst ($\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2/\text{La}^{3+}$). The effects of corncob-to-water ratio, reaction temperature and residence time on the performance of catalytic hydrothermal pretreatment were investigated. Results showed that the solid residues contained mainly lignin and cellulose, which was indicative of the efficient removal of hemicelluloses from corncob by hydrothermal method. The prepared catalyst with high thermal stability and strong acid sites originated from the acid functional groups was confirmed to contribute to the hydrolysis of polysaccharides into monosaccharides followed by dehydration into furfural. Highest furfural yield (6.18 g/100 g) could be obtained at 180 °C for 120 min with 6.80 g/100 g xylose yield when the corncob/water ratio of was 10:100. Therefore, selectively catalytic hydrothermal pretreatment of lignocellulosic biomass into important platform chemicals by solid acids is considered to be a potential treatment for biodiesel and chemical production.

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1. Introduction

Manufacture of fuels, energy products and chemicals from lignocellulosic biomass has been considered to be an environmentally friendly option to solve the problems derived from the

extensive utilization of fossil fuels (Romaní et al., 2010). However, it is necessary to modify or pre-treat lignocellulosic materials (LCMs) by physical and chemical approaches to satisfy the requirements of reducing the handling and transportation expenditures (Hoekman et al., 2011). Hydrothermal pretreatment (HTP) as a thermochemical procedure has become a candidate pathway for homogenizing feedstock to a certain degree and, thereby, minimizing handling and transportation challenges (Chang et al., 2013; Hoekman et al., 2011).

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HTP, also known as the wet torrefaction, has been considered as a cost-effective pretreatment with promising properties of limited equipment corrosion and simple operation (Chang et al., 2013; Romaní et al., 2010). The HTP process is carried out in water at elevated temperatures and pressures to partially break down the lignocellulosic structure of the feedstock, thereby recovering sugars and other chemicals and enhancing its suitability as a feedstock for subsequent thermochemical processing (Hoekman et al., 2011; Tang et al., 2012; Xiao et al., 2012a). In the subcritical region (100–374 °C), the ionization constant (k_w) of water increases with increasing temperature. When the temperature is higher than 150 °C, the H-bonding of H₂O starts weakening, then acid hydronium ions (H₃O⁺) form which can act as catalyst during the process (Ruiz et al., 2013).

Recently, the dehydration of carbohydrates from wood and non-wood feedstocks has been extensively studied (Choudhary et al., 2013; Sahu and Dhepe, 2012; Weingarten et al., 2011; Zhang et al., 2013). Furfural is a predominant chemical in the manufacture industries, which only can be produced from pentose in LCMs such as corncobs, oat hulls, and cottonseed hull bran catalyzed by acids (Zhang et al., 2013). It is a precursor used to synthesis organic materials such as furfuryl alcohol and furan chemicals such as furoic acid (Weingarten et al., 2010). Furfural derivatives also can be used as ingredients in the plastic, food, pharmaceutical and agricultural industries (Sánchez et al., 2013).

Intensive research endeavours have pursued the production of furfural by thermo-chemical processes using inorganic salts (Choudhary et al., 2012), metal oxides (Dias et al., 2007), solid acids (Choudhary et al., 2013) as well as ionic liquids (Serrano-Ruiz et al., 2012) as catalysts in monophasic (Campos Molina et al., 2012) and biphasic systems (Chheda et al., 2007). Among them, solid acid catalysts with the good thermal and chemical stabilities have been implemented in the furfural production process considering the environmental and economical issues.

The hemicelluloses fraction in LCMs can be depolymerized into oligomers and monomers in HTP process and further dehydrated into furan compounds (Ruiz et al., 2013). Under optimized conditions, hemicelluloses can be almost totally removed from LCMs in hot water, which need a lower temperature than that of cellulose (Vegas et al., 2008; Weiqi et al., 2012). The release of hemicelluloses from LCMs in the pretreatment process has the potential for furfural production. Studies reported on the HTP of LCMs so far have mainly focused on the further application of the solid products, while few efforts about the oriented conversion of the HTP liquid have been made. However, side-reactions may occur under harsh conditions to form oligomeric species (Dias et al., 2006). The addition of solid acid catalysts with high activity and selectivity is a desirable option for the highly efficient utilization of pretreatment liquid.

During recent years, increasing attentions have been directed towards utilizing corncob for bioenergy and bio-based materials by environmentally friendly approaches (Oh et al., 2013). Corncob is considered as a promising feedstock for xylose and furfural production due to its high pentosans and cellulose contents (Oh et al., 2013). The objective of the present work was to pre-treat corncob by catalytic hydrothermal method using solid acid (SO₄²⁻/TiO₂-ZrO₂/La³⁺) as a catalyst for the production of xylose and furfural. Pretreatment liquid was determined by high performance liquid chromatography (HPLC), high-performance anion-exchange chromatography (HPAEC). Chemical and physical characterizations of the solid residues obtained after the HTP of corncob were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), pore volume distributions and Brunauer-Emmett-Teller (BET) surface area, carbon-13 nuclear magnetic resonance (¹³C NMR), and elemental analysis.

2. Methods

2.1. Materials

Corncob used in this study was acquired from a farm in Shandong province, China. Prior to the HTP process, corncob was grounded into particles with a size of 40–60 mesh, and then oven-dried at 55 °C to constant weight. ZrOCl₂·8H₂O, TiCl₄, NH₄OH and La(NO₃)₃·6H₂O were purchased from Aladdin (China). The standard reagents of formic acid, levulinic acid, furfural and 5-hydroxymethylfurfural (HMF), L-arabinose, D-glucose, D-xylose, and D-galactose were purchased from Sigma-Aldrich. All reagents were used without any purification.

2.2. Preparation of SO₄²⁻/TiO₂-ZrO₂/La³⁺

The solid acid (SO₄²⁻/TiO₂-ZrO₂/La³⁺) was prepared by coprecipitation and impregnation methods (Li et al., 2010; Zhang et al., 2012). TiCl₄ (0.04 mol) and La(NO₃)₃·6H₂O in a required stoichiometric ratio of lanthanum to the target product (1.0 wt%) was added to ZrOCl₂·8H₂O (0.02 mol) solution slowly in an ice bath, respectively. The above solution was adjusted to pH in the range of 9–10 with concentrated ammonia and aged for 24 h to form Zr(OH)₄-Ti(OH)₄/La³⁺. The washed powder was dried at 110 °C for 24 h to form TiO₂-ZrO₂/La³⁺, and then impregnated with 1.0-M H₂SO₄ at the proportion of 15 mL/g for 6 h. The solid product was dried at 110 °C for 12 h and calcined at 550 °C for 4 h to get the target catalyst.

2.3. Selectively catalytic hydrothermal pretreatment of corncob

Experiments for selectively catalytic hydrothermal pretreatment of corncob were carried out in a 100-mL high-pressure batch reactor (SLM-100, Shenlang Co., Ltd., Beijing, China) at 160, 170, 180 and 190 °C in the range of 0–120 min, respectively. The apparatus contained a stainless steel pressure vessel (reactor), electric furnace used for heating the reactor, temperature controller, stirring equipment, pressure meter and air valve (Fig. S1, Supporting information). Corncob and water were mixed and ultrasounded for 30 min at room temperature to improve the dissolution rate of hemicelluloses from the corncob cell wall. The above mixture was transferred to the reactor and SO₄²⁻/TiO₂-ZrO₂/La³⁺ was added before the reactor was freed of oxygen by purging with nitrogen gas. Then the reactor was heated up to the desired temperature in a certain time period with magnetic agitator operating at 350 rpm/min. After the hydrothermal pretreatment, the reactor was cooled quickly with flowing water. Products were filtrated to get the liquid and solid fractions. The solid residue was washed with distilled water several times and dried for characteristic analysis. Each experiment was repeated twice under the same conditions to ensure the reproducibility of the results.

2.4. Analysis of liquid and solid products

2.4.1. Analysis of liquid products

Formic acid, levulinic acid, furfural and HMF were determined by HPLC (Waters 2414) equipped with a refractive index detector and a Bio-rad Aminex[®] HPX-87H (300 × 7.8 mm) column. 5 mM of H₂SO₄ was employed as the eluent with a 0.6 mL/min flow rate at 50 °C. Product yield was defined as gram from per 100 g of dry raw material (g/100 g).

Sugars were measured by HPAEC (Dionex ICS-3000, Sunnyvale, CA) with an amperometric detector and a guard PA-20 column

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