



Solid acid-induced hydrothermal treatment of bagasse for production of furfural and levulinic acid by a two-step process

Xiaohui Wang^a, Chunhui Zhang^a, Qixuan Lin^a, Banggui Cheng^a, Fangong Kong^b, Huiling Li^c, Junli Ren^{a,*}

^a State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

^b Key Laboratory of Pulp & Paper Science and Technology Ministry of Education, Qilu University of Technology, Jinan, Shandong 250353, China

^c Guangdong Key Laboratory for Innovative Development and Utilization of Forest Plant Germplasm, State Key Laboratory for Conservation and Utilization of Subtropical Agro-bioresources, South China Agricultural University, Guangzhou, 510642, China



ARTICLE INFO

Keywords:

Bagasse
Carbohydrate
Selective conversion
Furfural
Levulinic acid

ABSTRACT

A two-step process was developed to produce furfural and levulinic acid (LA) using the solid acid-induced hydrothermal treatment of bagasse. In the first step, hydrothermal pretreatment was applied to treat bagasse for producing furfural using Sn-MMT/SO₄²⁻ solid acids as catalysts in the biphasic system. In the second step, the treated residue was further hydrothermally treated for producing LA by the continuous use of solid acids. The hydrothermal treatment conditions were comparatively investigated, and the results showed that the highest yield of furfural was achieved up to 88.1% (170 °C, 2.4 h) in the first stage, and the yield of LA was 62.1% (180 °C, 3 h) in the second stage. Therefore, the two-step solid acid-induced hydrothermal treatments could make hemicellulose and cellulose of bagasse to be selectively fractionated and efficiently transformed into furfural and LA, respectively.

1. Introduction

With the aggravation of resource shortage and environmental pollution, a growing number of scientists have paid more and more attentions on the exploration of lignocellulosic biomass which is regarded as the potential alternative to fossil resource for the production of liquid fuels and chemicals (Carpenter et al., 2014). Lignocellulose with the complex physical structure mainly comprises cellulose, hemicellulose and lignin (Mosier et al., 2005). Among these components, cellulose and hemicellulose belong to carbohydrate, which account for 50%–80% of lignocellulosic biomass (Sun, 2010). Hemicellulose and cellulose could be acid-hydrolyzed into C5 and C6 sugars which could be transformed to the important platform compounds, such as furfural and levulinic acid (LA), which could be used for producing biofuel, plastic, pharmaceuticals and other products.

Furfural and LA, as two promising renewable platform compounds, could be produced by the acid-catalyzed hydrolysis of xylan-type hemicellulose and cellulose in lignocellulosic biomass such as corncob, straw and bagasse. For conventional industries, furfural and LA with the yields of about 40%–50% and 16%–60% (based on theoretical values), were produced using homogeneous mineral acids (HCl or H₂SO₄) as catalysts in the aqueous solution (Chang et al., 2007; De et al., 2011;

Karinen et al., 2011). However, homogeneous mineral acids may bring a few problems such as acid corrosion equipment, the difficult separation of catalysts from the reaction system, producing large amounts of acid wastewater. Heterogeneous solid acids appear to be more feasible than liquid acids in the catalytic hydrolysis of lignocellulosic biomass. Many research works have been done on solid acid-catalyzed hydrolysis of lignocellulose to furfural or LA in a one-step process. Furfural from lignocellulose could be achieved using solid acid catalysts such as SO₄²⁻/TiO₂-ZrO₂/La⁺, sulfonated porous polymer catalyst (SPTPA) and Sn-loaded montmorillonite (Sn-MMT) (Li et al., 2014, 2015; Zhang et al., 2017a). Also, LA was produced from lignocellulose using solid acid catalysts such as HY zeolite, zirconium phosphate (ZrP), and S₂O₈²⁻/ZrO₂-SiO₂-Sm₂O₃ (Chen et al., 2011; Weingarten et al., 2012; Ya'Aini et al., 2012). Although the high yield of furfural and LA could be obtained from lignocellulose using solid acids as catalysts, there are still many problems, for example, the transformation of only one component (hemicellulose or cellulose) in lignocellulose, the difficult separation of solid acids from treated lignocellulose and catalyst recycling (Li et al., 2014; Zhang et al., 2012). Thus, it is urgent to develop new approaches to make full use of hemicellulose and cellulose from lignocellulose in an environmentally sustainable manner.

Recently, various two-step catalytic treatment processes were

* Corresponding author.

E-mail address: renjunli@scut.edu.cn (J. Ren).

developed to produce furfural and glucose or to synthesize LA and xylose from lignocellulose, which could make hemicellulose and cellulose in the cell wall of lignocellulose to be selective fractionated and efficiently converted, respectively. An efficient pretreatment of *Eucalyptus* was conducted to produce furfural in the methyl isobutyl ketone/water biphasic system with formic acid as the catalyst, and the treated *Eucalyptus* was further converted into glucose by enzymatic hydrolysis in the second step (Zhang et al., 2017b). The yields of furfural and glucose were 82.0% and 57.7%, respectively. An efficient approach was proposed to selectively dissolve hemicellulose and cellulose of *Quercus mongolica* to produce xylose and LA using dilute sulfuric acid as the catalyst (Jeong et al., 2016). It was found that 15.6 g/100 g of xylose was obtained in the first step at 150 °C and 16.5 g/100 g of LA was achieved in the second step at 200 °C. A two-step process was brought forward for the selective dissolution and conversion of carbohydrates in bagasse using methane-sulfonic acid as the catalyst, in which 11.7 g/L xylose and 67.7 mol% LA were gained after the first step treatment (thermal and enzymatic treatment) and the second step treatment (acid catalyzed hydrolysis), respectively (Schmidt et al., 2017). Although the high yields of target products (furfural and glucose, LA and xylose) are obtained by these efficient two-step treatments, there still are the non-ignorable problems such as the acid corrosion equipment, the difficulty in separation of catalyst and target products and so on.

In our previous work, it was found that the SnCl₄ presented the high catalytic performance for the production of furfural. 63.0% and 78.1% of furfural yields were achieved from xylose (130 °C-6 h), and xylan-type hemicellulose (150 °C-2 h), respectively (Wang et al., 2015). In order to improve its stability and the recovery, SnCl₄ was loaded on montmorillonite (MMT) by ionic exchange method under microwave irradiation, followed by sulfuric acid impregnation to form a new catalyst Sn-MMT/SO₄²⁻ (Lin et al., 2017). This new catalyst displayed the high catalytic activity and the excellent recyclability in the conversion of xylose to furfural, and the highest yield of furfural was achieved up to 79.64%. Thus, using Sn-MMT/SO₄²⁻ to replace liquid acid in the treatment of lignocellulose could solve the problems of the difficulty of catalyst reuse and the acid corrosion equipment. After the treatment of lignocellulose, the targeted furfural from xylan-type hemicellulose could be obtained in the hydrolysate, and treated lignocellulose containing cellulose and lignin and solid acid could be further treated into other products without the separation of solid acids. However, up to now, there is no study reported in the literature on the two-step solid acid-induced treatment of lignocellulose to produce different important platform chemicals.

In this work, the objective was to develop a highly efficient two-step treatment approach for producing furfural and LA from bagasse via the continuous use of Sn-MMT/SO₄²⁻ solid acids as catalysts, in which xylan-type hemicellulose was selective fractionated from bagasse and further converted into furfural in the first step, and the solid fraction (treated bagasse and solid acids) was further treated at an elevated temperature for the production of LA in the second step. This approach was environment friendly and could make the main components (hemicellulose and cellulose) of bagasse to be selectively fractionated and efficiently converted. After the two-step treatment, the residue containing lignin and solid acids could be further transformed into carbon-based catalysts or energy gas by carbonization or pyrolysis.

2. Materials and methods

2.1. Materials

The bagasse was obtained from Guangzhou Sugarcane Industry Research Institute (Guangzhou, China), which was ground into 40–60 mesh particles and oven-dried at 80 °C for 12 h to remove water. Bagasse was extracted with acetone/ethanol (2:1, v/v) for 6 h by Soxhlet apparatus to remove wax and other impurity before use. The

main compositions of wax-free bagasse were as follows: cellulose 43.0 wt%, hemicellulose 28.8 wt% (25.8 wt% xylose, and 3.02 wt % arabinose) and lignin 18.3 wt%. Standard reagents of furfural (HPLC, ≥99.0%) and LA (HPLC, ≥99.0%) were provided by Sigma-Aldrich. SnCl₄·5H₂O (AR, ≥99.0%) and MMT (GR, 98%) were purchased from Chengdu Gracia Chemical Technology Co., Ltd., (Chengdu, China). Dichloromethane (DCM, AR, ≥99.5%), Methylisobutylketone (MIBK, AR, ≥99.5%), Tetrahydrofuran (THF, AR, ≥99.0%), Methylbenzene (MB, AR, ≥99.5%) were provided by Guanghua Sci-Tech Co., Ltd., (Guangzhou, China). Gamma-butyrolactone (GBL, AR, ≥98%), P-xylene (PX, AR, and ≥99%), Dimethyl sulfoxide (DMSO, AR, ≥99.5%), 2-Methyltetrahydrofuran (2-MTHF, AR, ≥99.5%) and other reagents were obtained from Tianjin Kermel Chemical Regent Co., Ltd., (Tianjin, China).

2.2. Preparation of solid acid catalyst

Sn-MMT/SO₄²⁻ was prepared referring to the method in the literature (Lin et al., 2017). In a typical synthesis, 4 g of MMT and 196 mL of distilled water were added to the triangulation flask with vigorous magnetic stirring at the speed of 1000 r/min for 30 min at 25 °C, followed by standing for 24 h. Then, the SnCl₄ solution of 0.34 M (20 mL) was dropped slowly and the mixed solution was treated for 2 h at 85 °C under microwave irradiation (800 W, 500 r/min). The solid (Sn-MMT) was washed with distilled water until chloride ions were not detected in the washing liquid by the AgNO₃ solution, and then dried at 105 °C overnight, followed by being ground to powder in a mortar with a pestle. Subsequently, 1 g Sn-MMT and 20 mL of 1 mol/L H₂SO₄ were mixed at 30 °C and stirred for 6 h. After that, the solids were filtered and washed until the SO₄²⁻ was not detected by BaCl₂ in the washing water, and the washed solid was dried to obtain sulfonated Sn-MMT (Sn-MMT/SO₄²⁻).

2.3. The hydrothermal treatment of bagasse for furfural and LA production

2.3.1. Furfural production in the first stage

Experiments of the solid acid-induced hydrothermal reaction were conducted in a stainless-steel autoclave (KH-25 Gongyi Yuhua Instrument Co., Ltd., Henan, China) at 160 °C, 170 °C, and 180 °C within a time range of 1–3 h, respectively. Bagasse was suspended in the biphasic system and the monophasic system (Table 1) with a 1:50 (g/mL) rate of solid to liquor. Subsequently, Sn-MMT/SO₄²⁻ catalysts were added. The stainless-steel autoclave reactor was heated, and the

Table 1

The conversion of bagasse to furfural with different co-solvents systems.^a

Entry	Catalyst	Inorganic phase	Organic phase	Furfural yield (%)		
				Inorganic	Organic	Total
1	–	H ₂ O	–	7.89	–	7.89
2	–	H ₂ O	DCM	2.68	6.16	8.84
3	SnCl ₄ ·5H ₂ O	H ₂ O	DCM	5.32	17.79	23.11
4	MMT	H ₂ O	DCM	4.87	16.85	21.72
5	Sn-MMT	H ₂ O	DCM	7.48	38.83	46.31
6	Sn-MMT/SO ₄ ²⁻	H ₂ O	DCM	11.35	51.17	62.52
7	Sn-MMT/SO ₄ ²⁻	NaCl ^b	DCM	1.12	67.6	68.72
8	Sn-MMT/SO ₄ ²⁻	NaCl ^b	MIBK	1.32	60.32	61.64
9	Sn-MMT/SO ₄ ²⁻	NaCl ^b	PX	3.12	47.73	50.85
10	Sn-MMT/SO ₄ ²⁻	NaCl ^b	MB	2.17	52.15	54.32
11	Sn-MMT/SO ₄ ²⁻	NaCl ^b	2-MTHF	1.13	49.88	51.01
12	Sn-MMT/SO ₄ ²⁻	NaCl ^b + DMSO		62.33		62.33
13	Sn-MMT/SO ₄ ²⁻	NaCl ^b + GBL		63.91		63.91
14	Sn-MMT/SO ₄ ²⁻	NaCl ^b + THF		62.74		62.74

^a Reaction conditions: Bagasse 0.2 g, catalyst 0.1 g, V_O:V_I = 1:1, 160 °C, 2 h; V_O and V_I represents the volume ratio of organic phase and inorganic phase, and the total volume was 10 mL.

^b NaCl: Saturated sodium chloride solution.

Download English Version:

<https://daneshyari.com/en/article/8879551>

Download Persian Version:

<https://daneshyari.com/article/8879551>

[Daneshyari.com](https://daneshyari.com)