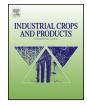Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Furfural production from biomass–derived carbohydrates and lignocellulosic residues via heterogeneous acid catalysts

Luxin Zhang [a,*], Guoyun Xi [a], Kun Yu [b], Han Yu [b], Xiaochang Wang [a]

[a] College of Environmental and Municipal Engineering, Key Lab of Northwest Water Resource, Environment and Ecology, MOE, Key Laboratory of Environmental Engineering, Shaanxi, Xi'an University of Architecture and Technology, Xi'an 710055, PR China
[b] College of Environmental Science and Engineering, Nankai University, Tianjin 300071, PR China

ARTICLE INFO

ABSTRACT

With the aim to enhance the efficiency of the furfural production from lignocellulosic biomass, different catalysts, such as montmorillonite, heteropolyacids, silicoaluminophosphates, and modified beta zeolites, were studied for catalysis of the conversion of biomass–derived carbohydrates and raw biomass into furfural in lactone solvents. Interestingly, we obtained atypical results showing that modified beta zeolites convert glucose and cellulose into furfural as the predominant product. Furfural formation from corncob, sugarcane bagasse, xylose/glucose mixtures, and xylan/cellulose mixtures were also studied. Al–beta was found to display high activity for the conversion of corncob and bagasse in γ-valerolactone (GVL), giving furfural yields of up to 51.1% and 40.9% (molar yields based on both cellulose and xylan content), respectively. The catalytic route proposed in this paper showed a great potential for co–converting hemicellulose and cellulose in the furfural production from lignocelluloses.

1. Introduction

Lignocellulosic materials are the renewable and most abundant key feedstock for the production of bio–based products. Among products derived from lignocellulosic biomass, furfural displays interesting properties as building–block for the production of high value–added products (Peleteiro et al., 2016; Zeitsch, 2000). Furfural is widely used in the fields of pharmaceuticals, plastics, pesticides, oil refining, organic synthesis, and the production of non-petroleum polymeric materials and has been ranked as one of the "top 10" bio–based products from biorefinery carbohydrates in the U.S. Department of Energy report (Agirrezabal-Telleria et al., 2014a; Bozell and Petersen, 2010). Furthermore, furfural derivatives also present important organic intermediates with a wide range of applications (Hoydonckx et al., 2007; van Putten et al., 2013a,b).

The artificial synthesis of furfural is cost ineffective. Furfural is industrially produced by lignocellulosic biomass (such as corncob, sugarcane bagasse, oat hulls, cottonseed hulls, etc.) hydrolysis and pentose dehydration using sulfuric acid as catalyst. A large amount of superheated steam is also used as heat supply and stripping agent for furfural. The commercial furfural production process suffers from disadvantages such as low yields, high energy–consumption, and equipment corrosion. Furthermore, a great deal of solid residues (furfural residues, mainly composed of cellulose (~45%) and lignin, and are acidic due to the remaining H_2SO_4) are excreted at high humidity and temperature (Chang et al., 2015; Xing et al., 2015), and pre–treatment steps consuming a huge amount of water, alkali, or other organic solvents are often required for using furfural residues (Atilio de Frias and Feng, 2014; Lin et al., 2014). Challenges associated with the sustainable growth of the furfural industry as well as the improvement of chemical technology for furfural production continue to be of great importance.

Investigations for optimizing the furfural production deal with both batch and continuous processes comprising simultaneous furfural stripping (Zeitsch and Tepohl, 2004), simultaneous furfural extraction in biphasic systems (Gürbüz et al., 2012) or asynchronous furfural extraction, and encouraging furfural yields were achieved in these systems. Recent studies focus on the design of novel processes and the development of efficient, easy–to–separate, and water–tolerant catalysts. Furthermore, the development of reaction media for the formation of furfural has also been intensively investigated (Gómez Bernal et al., 2014). Current alternative approaches involve the use of mineral acids, metal halides (Mao et al., 2013; Wang et al., 2015; Zhang et al., 2013), metal oxides (Molina et al., 2015; Weingarten et al., 2011), as well as acidic solid materials (Agirrezabal-Telleria et al., 2014b;

* Corresponding author.
  E-mail address: zhangluxinxx@126.com (L. Zhang).

Chen et al., 2015; Xu et al., 2015; Kaiprommarat et al., 2016) as catalysts in either monophasic (e.g., water, ionic liquids, or organic solvents) or biphasic systems (e.g., water/organic solvent or organic solvent/organic solvent), such as H_2SO_4 in water/THF (Xing et al., 2011), metal halides in water/toluene (Enslow and Bell, 2015), SAPO–44 in water/toluene (Bhaumik and Dhepe, 2015), SO_4^{2-}/TiO_2–ZrO_2/La^{3+} in water/MIBK (Li et al., 2014), MgF_2 in water/toluene (Agirrezabal-Telleria et al., 2013), Sn–MMT in SBP/DMSO (Li et al., 2015), NBO in water/CPME (Molina et al., 2015), Glu–TsOH–Ti in water/MeTHF (Mazzotta et al., 2014), and so on. In addition, approaches using neither mineral acids nor heterogeneous catalysts for the furfural production from xylose and hemicellulose hydrolysates have also been studied. Morais et al. developed a novel route by employing high–pressure CO_2 as catalyst, affording furfural yields in the range of 43–70% (Morais and Bogel-Lukasik, 2016; Morais et al., 2016). Furthermore, acidic ionic liquids used as both catalyst and reaction solvent, giving moderate to high furfural yields in biphasic systems (Lima et al., 2009; Peleteiro et al., 2015a; Peleteiro et al., 2015b), also attracted some interest.

Most studies on furfural production focus on hemicellulose derived sugars. Although these studies improved the furfural yield, the amount of furfural residue was still large, as only hemicellulose derived sugars from lignocellulosic biomass were used. Regarding the material balance, the furfural yield improves significantly if the cellulose fraction in lignocelluloses can also be converted into furfural. It is generally believed that hexoses undergo dehydration to form 5–HMF (van Putten et al., 2013a), whereas pentoses undergo dehydration to form furfural. However, furfural was also obtained with or without adding catalyst during the conventional hydrothermal treatment processes of glucose or cellulose (Aida et al., 2007; Alonso et al., 2013; Jin and Enomoto, 2011), and some earlier studies found that the catalytic fast pyrolysis of glucose (Jae et al., 2011) or cellulose (Kawamoto et al., 2007) gave furfural as the predominant product with furfural yields of 23–40%. In addition, Dumesic et al. obtained a furfural yield of 37% in the conversion of glucose in γ–valerolactone (GVL) upon H–beta zeolite catalysis (Gürbüz et al., 2013). Cui et al. reported that H–beta–catalyzed conversions of fructose, glucose, and cellulose in γ–butyrolactone reached furfural yields of 63.5, 56.5, and 38.5%, respectively (Cui et al., 2016). Furthermore, we previously investigated the catalytic effect of metal salts on the furfural formation from glucose and cellulose in GVL, attaining furfural yields in a range of 11–24% depending on the structure of the feedstocks (Zhang et al., 2014). However, although we obtained improved furfural yields, recovery and recycling of the inorganic salts remains difficult, thus an effective and easily separable catalyst is still needed.

The present work continues to study the furfural production from biomass, especially from the cellulose fraction, whereas only hemicellulose in lignocelluloses can be commercially used in the acid–catalyzed approach. If the cellulose fraction of the raw materials can be selectively converted into furfural via the same catalysis step, the efficiency of the furfural production from biomass will be significantly enhanced. The presented efficient catalytic pathway for furfural production via the integrated conversion of hemicellulose and cellulose in lignocelluloses constitutes the novelty of this work.

2. Materials and methods

2.1. Materials

D–xylose (≥98%), $H_3O_{40}PW_{12}$, xylan and lactone solvents were purchased from Macklin. Microcrystalline cellulose (average particle size 50 μm) was supplied by Acros. H–Beta zeolite and D–glucose (≥99%) were supplied by Alfa Aesar. $H_4[Si(W_3O_{10})_4]\cdot xH_2O$ and montmorillonite K–10 were purchased from Aladdin. Silicoaluminophosphates (SAPO–5 and SAPO–11) were supplied by Shanghai Shentan Co., Ltd. (Shanghai, China). Al–Beta, Fe–Beta and Cr–Beta were prepared following the procedures in the literatures with some slight modifications (see Supporting information for the preparation and characteristics of the metal modified beta zeolites). Other reagents were supplied by Tianjin Kermel Chemical Co., Ltd. (Tianjin, China). All the commercial chemicals were used as received without further purification.

The corncob used in this study was obtained from Xiqing District, Tianjin, China. Sugarcane bagasse was collected from Beilin District, Xi'an, China. After air–drying, the corncob or sugarcane bagasse was ground using a high–speed rotary cutting mill equipped with three blades, and then sieved to pass 80 mesh, and dried in a vacuum drying oven at 378 K to a constant weight before experiments.

2.2. Procedure for the conversion of different feedstocks into furfural

Standard procedure for furfural formation started by different feedstocks: required amount of solvent, catalyst and feedstock were loaded into a thick–walled glass vessel (8 mL) and then sealed, the dosage weight ratios were based on GVL. The reaction mixture was then heated in a preheated oil bath at specified temperature and time. A magnetic stirrer was used for mixing during the reaction. After the required residence time, the reaction was ended by quenching the reactor in an ice bath immediately. Samples were then diluted, filtered and analyzed using HPLC. Each experiment was performed in triplicate, and data are expressed as mean ± standard deviation.

2.3. Quantification procedure for products

Quantitative analysis of xylose and glucose was performed by using HPLC (Shimadzu LC–2010AHT) equipped with a refractive index detector and an aminex HXP–87H column, a solution of H_2SO_4 (5 mmol/L) was used as the mobile phase at a flow rate of 0.6 mL/min, and the column temperature was maintained at 338 K. The concentration of furfural and 5–HMF was determined with a XDB–C18 column and a UV detector, a solution of acetonitrile/water (15/85, v/v) was used as the mobile phase at a flow rate of 1 mL/min, and the column temperature was maintained at 303 K. Yields of the products were calculated on molar basis defined as follows (the amount of glucose and xylose units was determined according the method of NREL (NREL, 2008a,b), see references for details):

$$\text{furfural yield (from glucose, mol\%)}$$
$$= \frac{\text{moles of furfural produced}}{\text{moles of starting glucose}} \times 100$$

$$\text{HMF yield (from glucose, mol\%)}$$
$$= \frac{\text{moles of HMF produced}}{\text{moles of starting glucose}} \times 100$$

$$\text{furfural yield (from cellulose, mol\%)}$$
$$= \frac{\text{moles of furfural produced}}{\text{moles of glucose unit}} \times 100$$

$$\text{HMF yield (from cellulose, mol\%)}$$
$$= \frac{\text{moles of HMF produced}}{\text{moles of glucose unit}} \times 100$$