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Note

Production of furfural from xylose at atmospheric pressure by dilute sulfuric acid and inorganic salts

Chunguang Rong, Xuefeng Ding*, Yanchao Zhu, Ying Li, Lili Wang, Yuning Qu, Xiaoyu Ma, Zichen Wang

College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

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ABSTRACT

In this paper, the dehydration of xylose to furfural was carried out under atmospheric pressure and at the boiling temperature of a biphasic mixture of toluene and an aqueous solution of xylose, with sulfuric acid as catalyst plus an inorganic salt (NaCl or $FeCl_3$) as promoter. The best yield of furfural was 83% under the following conditions: 150 mL of toluene and 10 mL of aqueous solution of 10% xylose (w/w), 10% H_2SO_4 (w/w), 2.4 g NaCl , and heating for 5 h. $FeCl_3$ as promoter was found to be more efficient than NaCl. The addition of DMSO to the aqueous phase in the absence of an inorganic salt was shown to improve the yield of furfural.

Rapidly growing worldwide energy demand has triggered a renewed interest in producing fuels from biomass to add to worldwide energy supplies. Renewable biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates.[1] The challenge for the effective utilization of these sustainable resources is to develop cost-effective processing methods to transform highly functionalized carbohydrate moieties into value-added chemicals.[2] Biomass is made up of four major components: cellulose, hemicellulose, lignin, and starch. Hemicelluloses are the second most abundant plant material after cellulose. The hemicellulose present in biomass undergoes hydrolysis in acidic media to form xylose (pentose), and then xylose is dehydrated to form furfural. There is no synthetic route available for furfural production; therefore furfural is exclusively produced from renewable biomass resources by acid-catalyzed dehydration of pentoses. Due to its unsaturated bonds and aldehyde group, furfural is a highly versatile and key derivative used in the manufacture of a wide range of important chemicals, and it is likely to be of increasing demand in different fields, such as oil refining, plastics, pharmaceutical, and agrochemical industries.[3] In addition, researchers have recently shown that HMF and furfural can serve as precursors for production of liquid alkanes (C_7–C_{15}) that serve as diesel fuel components.[2] About 250,000 tons of furfural, probably the only unsaturated, large volume, organic chemical, are prepared from carbohydrate sources annually.[4]

The industrial technology for furfural production relies on batch or continuous reactors where the pentosan fraction of the lignocellulosic is converted into monosaccharides (pentoses) by acid hydrolysis. Further dehydration reactions of the pentoses yield furfural. The feedstock is loaded to the digester and mixed with an aqueous solution of inorganic acids. The system is maintained at the desired reaction temperature by adding steam to the digester. Furfural is continuously extracted from the reactor by steam distillation to minimize its loss through secondary reactions of degradation and condensation. The concentration of furfural in the reactor outlet stream is around 3% (w/w), and it is recovered in a series of distillation columns. Depending on the configuration of the separation process, methanol and acetic acid may also be obtained as marketable byproducts. At the end of the reaction period, the solid residue is separated from the liquid, which may be processed to recover the acid catalyst. The residual solid is made up of lignin and depolymerized cellulose, and this solid may be dried and burned in a boiler to provide steam for the plant. Normally, when batch reactors are used, several digesters are operated in coordinated rotation so that the distillation plant can be operated continuously. Typical reaction conditions are 3% ($W_{acid}/W_{solution+lignocellulosic}$) sulfuric acid, an acid solution to lignocellulosic mass ratios of between 2:1 and 3:1, reaction temperatures of around 170–185 °C, and reaction times of 3 h. With this technology, maximum furfural yields are between 45% and 50% of the potential.[5]

In the early work, researchers used corncob and corn stover for furfural production.[6,7] Recently, a few investigations involving cyclodehydration of xylose in liquid phase using various

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* Corresponding author. Tel./fax: +86 431 85155358.
E-mail address: dingxf@jlu.edu.cn (X. Ding).

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homogeneous or solid acid catalysts have been reported. Scientists have studied the dehydrocyclization of xylose into furfural using acid catalysts, including mineral acids, zeolites, acid-functionalized MCM materials, and heteropolyacids, sulfated zirconia, exfoliated titanate, niobate, and titanoniobate nanosheets, mesoporous silica-supported 12-tungstophosphoric.[3,8–13] Morin et al. also reported the dehydration of xylose over (H^+) mordenite, using a continuous two-liquid phase (aqueous-toluene) flux in a plug-flow reactor at 260 °C and 55 atm, with a 98% conversion rate, a 98% furfural molar yield, and a 98% furfural selectivity.[14] Solid acid has a lot of advantages, but its synthesis is very complicated. Also it is costly and prone to inactivation. The experiments which use heterogenous catalysts (solid acids) usually need special conditions, so the application field of solid acids is constricted.

The present study deals with production of furfural from xylose. To our knowledge, there are few studies about the dehydration of xylose to furfural at atmospheric pressure. Only early scientists studied the dehydration of xylose with hydrochloric acid.[15,16] No reports about vast scale organic solvent extracting furfural production from xylose with mineral acid and inorganic salts at atmospheric pressure exist. Our experimental condition was very mild. Therefore, optimization of dilute sulfuric acid catalyst for the production of furfural from xylose was performed in a biphasic system with quantity of organic extraction solvent, initial xylose concentration, and acid concentration as the major factors to consider. And we chose toluene as an organic extraction solvent because furfural had good solubility in it.

The ratio of extracting solvent (toluene) to aqueous system affected the yield of furfural. The results of mineral acid dehydration of xylose in biphasic systems are presented in Figure 1. When the ratio of toluene/water was 100:77 (V/V), the yield of furfural was only 14%. With the ratio of toluene/water increased to 100:10 (V/V) and 150:10 (V/V), the yields became 21% and 33%, respectively. When the ratio reached to 175:10 (V/V), the yield increased to 43%.

The experiment was performed by stirring the biphasic system with high speed. Water was dispersed in toluene. Each aqueous drop could be regarded as a small reactor. The surface of aqueous contacted with the organic phase completely. As the ratio of toluene/water (100:77) became lower, aqueous drop was bigger comparatively which caused low yield of furfural. When the ratio was enhanced to 150:10 (V/V) or 175:10 (V/V), aqueous drop became much smaller, which showed great character and resulted in high yield of furfural. Furfural was produced in aqueous drop, and then it was immediately extracted to the organic phase. Some side reactions were avoided, which could decrease the yield of furfural.

Figure 2 shows the effect of concentration of sulfuric acid on the selectivity for dehydration of xylose and on the yield of furfural while using NaCl as the promoter. The experiments were conducted in water using toluene as an extracting solvent. The yield of furfural was higher in high concentration of sulfuric acid systems compared to that in low concentration. The best furfural yield was 75% achieved with 10% (w/w) acid after a 5-h reaction time. For xylose dehydration to furfural, the yield under 10% acid was nearly a ninefold improvement than that under 2.5% (w/w) acid. But when the concentration of sulfuric acid became 12.5% (w/w), the yield reduced to 51%. The rate of xylose dehydration increased with increasing the concentration of H^+. The low yields of furfural with 12.5% (w/w) acid could be attributed to side reactions, such as xylose dehydration to other aldehydes (e.g., formaldehyde), degradation of furfural, or polymerizations of intermediate, and furfural. In addition, xylose forms oligosaccharides, which contain reactive hydroxyl groups leading to higher rates of cross polymerizations with reactive intermediates and furfural.

Different concentrations of xylose were researched at 150:10 (V/V) toluene/aqueous, with 10% acid for 5 h. The amount of NaCl as promoter was 1.2 g. The best furfural yield achieved was 75% at 10% (w/w) xylose (Fig. 3), which had been detected with change of acid conditions. When the concentration of xylose was higher than 10%, the yield of furfural reduced to 68% and 66%. The decrease of furfural yield was not very rapid.

Previous studies have shown that the inorganic salts enhanced xylose monomer and xylotriose degradation;[17] also chloride ions enhanced furfural formation from D-xylose.[18] But their studies were performed in hermetic systems and under certain temperatures. In our study, dehydration experiments were conducted at atmospheric pressure with NaCl and $FeCl_3$ as addition agents. The adding of NaCl increased the yield of furfural from 20% to 43% with 175:10 (V/V) toluene/aqueous at 10% xylose, 5% acid for 5 h (Fig. 4a). Then the amount of NaCl was tested to show the effect on the yield of furfural. Furfural yield increased along with the amount of NaCl increase. The yield reached nearly 83% when

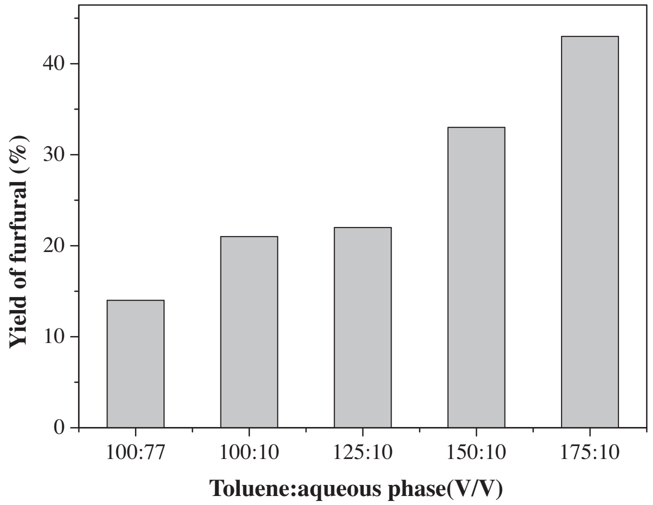

Figure 1. Effect of the toluene-to-aqueous phase ratio (V/V) on the furfural yield under the following conditions: 10% xylose (w/w), 5% H_2SO_4 (w/w), 1.2 g NaCl, heating for 5 h.

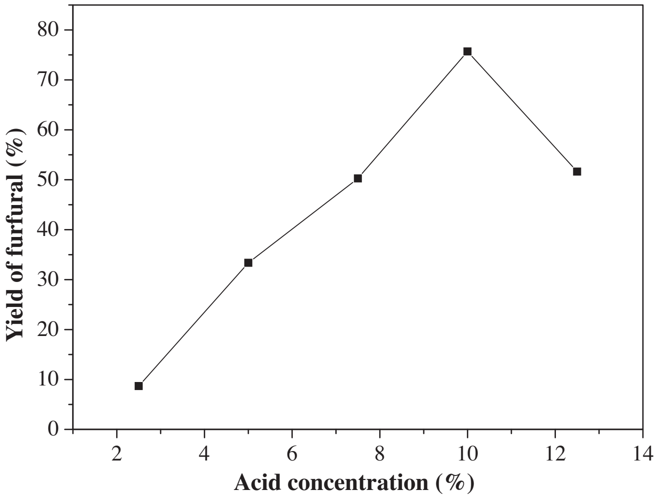

Figure 2. Yield of furfural at different sulfuric acid concentrations under the following conditions: 150 mL of toluene, 10 mL of an aqueous solution of 10% xylose (w/w), 1.2 g NaCl, heating for 5 h.

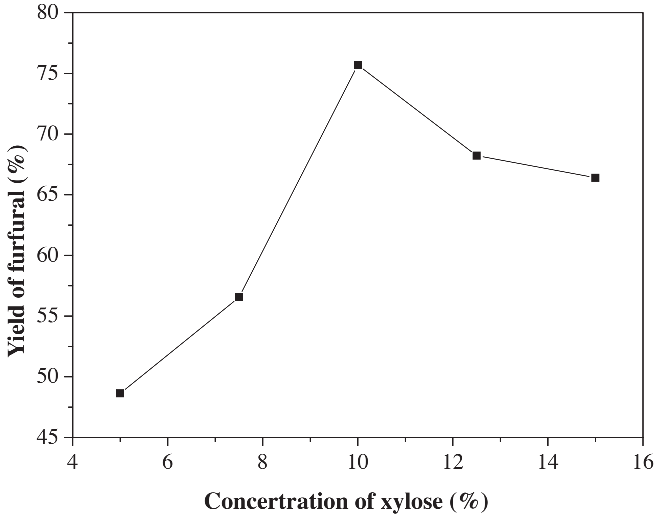

Figure 3. Effect of changing initial concentration of xylose on furfural yield under the following conditions: 150 mL of toluene, 10 mL of an aqueous solution of 10% H_2SO_4 (w/w), 1.2 g NaCl, heating for 5 h.

the amount of NaCl was 2.4 g at the toluene/aqueous ratio of 150:10 (V/V) with 10% xylose and 10% sulfuric acid (Fig. 4a). We further studied the effect of changing the inorganic salt from NaCl to $FeCl_3$. As seen in Figure 4b, the yield of furfural is 45% with 0.6 g $FeCl_3$, higher than with 0.6 g NaCl. At atmospheric pressure, $FeCl_3$ also promoted furfural formation from D-xylose better than NaCl. When $FeCl_3$ was used only as catalyst without sulfuric acid added, the yield of furfural was very low (5%) with 10% xylose for 5 h. Single $FeCl_3$ without acid had poor advancement in xylose dehydration to furfural. Although $FeCl_3$ alone could serve as catalyst accelerator at atmospheric pressure, it could not substitute sulfuric acid in these experiments.

The addition of electrolytes to the aqueous could generally induce significant changes by attracting or orienting its molecules, or by changing its ordered short range structure and in general by its interaction with the solute. In the same way, these effects could be regarded as responsible factors for the reported results in terms of xylose reaction rates and furfural yield. Furthermore, when compared the results for $FeCl_3$ with those for NaCl, it can be noticed that the nature of the ions is very important. Thus a direct contribution of the ions to the chemistry of the reaction could be considered to play a major role.

Earlier work has suggested that DMSO improved selectivities and dehydration rates in formation of 5-hydroxymethylfurfural (HMF). There was similarity between the formation of furfural from xylose and the formation of HMF from glucose, so we studied the effects of varying the DMSO level in the aqueous phase. Xylose dehydration was conducted at a constant acid concentration, equal to 10%, and 10% xylose in the presence of toluene as an extracting solvent after 2 h. As seen in Figure 5, DMSO was added to a level of 3:7 (V/V) DMSO/water, which improved the yield from 20% to 30%, with a further increase in yield to 46% for 5:5 (V/V) DMSO/water.

Previous study has suggested that DMSO suppresses both the formation of condensation byproducts and the HMF rehydration by lowering the overall water concentration. So it could be speculated that DMSO could play the same role in furfural production. DMSO also changed the form of xylose in water, which may profit the formation of furfural, as the furanose form of glucose upon adding DMSO.[2]

This work demonstrates that a biphasic system at which the ratio of organic phase to aqueous phase was larger than 10:1 could be tuned to process xylose to produce furfural. All the experiments were operated at atmospheric pressure and biphasic system azeotropy. The process variables that influence the yields of furfural are the ratio of toluene to water, the concentration of sulfuric acid, the DMSO content in aqueous phase, the initial sugar concentration, and the amount of inorganic salt. The yield of furfural reached nearly 83% when NaCl was 2.4 g at the toluene/aqueous ratio of 150:10 (V/V) with 10% xylose and 10% sulfuric acid. The concentration of acid was considered to play the major role on the yield of furfural. The results showed that inorganic salts could enhance the reaction of xylose to furfural in aqueous acidic solution at atmospheric pressure, especially $FeCl_3$.

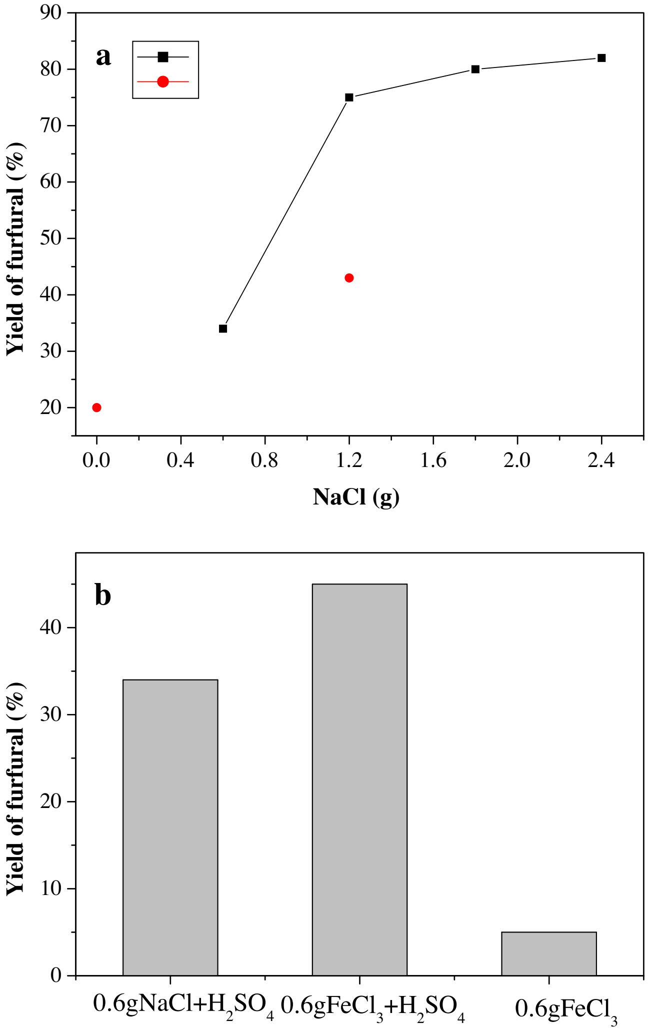

Figure 4. (a) Effect of amount of NaCl on furfural yield. The red points represent the furfural yield for dehydration in water aqueous with 175:10 (V/V) toluene/aqueous at 10% xylose (w/w), 5% H_2SO_4 (w/w) for 5 h. The black line represent the furfural yield for dehydration in water aqueous with 150:10 (V/V) toluene/aqueous at 10% xylose (w/w), 10% H_2SO_4 (w/w) for 5 h. (b) Effect of $FeCl_3$ on furfural yield under the following conditions: 150 mL of toluene, 10 mL of an aqueous solution of 10% xylose (w/w), 10% H_2SO_4 (w/w), heating for 5 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

1. Experimental section

1.1. Materials and experimental methods

1.1.1. Materials

All chemical reagents, such as xylose, sulfuric acid, toluene, ferric trichloride and sodium chloride, etc. were of analytical grade and obtained from Sinopharm Chemical Regent Co. Ltd in PRC.

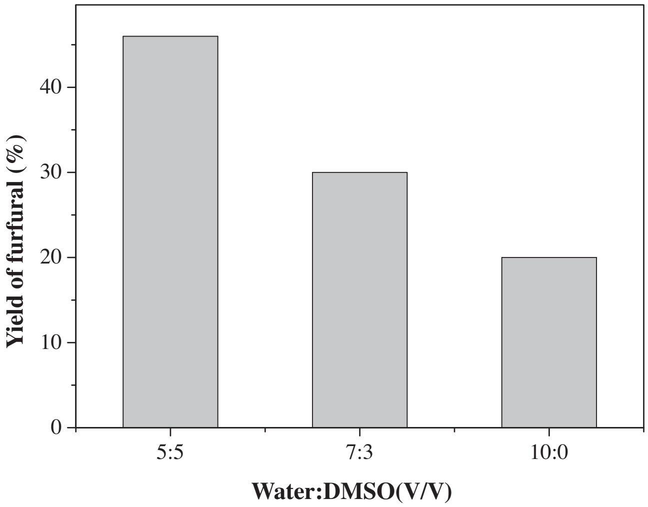

Figure 5. Effect of DMSO content in water/DMSO (V/V) mixture on yield of furfural under the following conditions: 150 mL of toluene, 10 mL of an aqueous solution of 10% xylose (w/w), 10% H_2SO_4 (w/w), 1.2 g NaCl, heating for 2 h.

1.1.2. Methods

All dehydration reactions were carried out in a two-phase batch reactor system containing a reactive aqueous layer and an extracting organic layer. All experiments were conducted using a glass flask, which was heated in a heating jacket as a batch reactor with a working volume of 250 mL. In a typical experiment, 10 mL of aqueous phase solution to which NaCl (or $FeCl_3$), xylose, and H_2SO_4 as acid catalyst were added and 100 mL of organic phase solution were poured into the reactor. The reactor was placed in a heating jacket until boiling for the time specified. After reaction, the reactor was cooled to room temperature by flowing air.

1.2. Analytical procedures

The sugars were analyzed using HPLC (Hewlett–Packard, Agilent 1100, 23 USA) with a Zorbax-NH_2 column (4.6 × 250 mm, 5-Micron, Agilent, USA) combined with an RI detector. The mobile phase was acetonitrile and water in a ratio of 75:25 (v/v), the operating temperature was controlled at 25 °C, and the flow rate was set at 0.72 mL/min. Standard sugars were run under the same conditions.

Furfural (or furaldehyde) was analyzed by GC–FID (HP 6850, Hewlett–Packard) using a StabilwaxÒ-DA column. The flow rate of helium was 1.2 mL/min. The temperatures of injection port and detection port were 230 °C and 250 °C, respectively. The injection volume was 1 mL. The initial temperature of the oven was 70 °C for 1 min, followed with a ramp of 20 °C/min to final temperature of 180 °C and then held for 2 min. Under these conditions furfural has a retention time of 5.9 min.

1.3. Calculations

Xylose concentration refers to the aqueous phase concentration because no xylose was present in the organic phase. Furfural yield was calculated as given below.

$$Yield = \frac{M_{furfural,obtain}}{M_{furfural,potential}}$$

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