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Microwave-assisted dehydration of *D*-xylose into furfural by diluted inexpensive inorganic salts solution in a biphasic system

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ABSTRACT

Production of furfural from biomass using less corrosive acids and minimizing the formation of undesired by-products is great challenge. Dehydration of *D*-xylose to furfural was carried out under microwave irradiation in biphasic system consisting of CPME and aqueous inorganic salts solution. Best conditions of dehydration of *D*-xylose using $FeCl_3$ were investigated by varying temperature, reaction time, pentose loading and influence of NaCl. Highest furfural yield of 74% was achieved at 170 °C for 20 min in presence of 10 mol% of iron chloride and 100 mol% of sodium chloride in water-CPME, 1:3, v/v. Addition of NaCl was found to increase the catalytic activity of $FeCl_3$ and allowed to reduce the amounts of $FeCl_3$ used from 20 mol% to 10 mol%. This approach was tested with success starting from *L*-arabinose and xylan, a pentose-rich polysaccharide.

1. Introduction

Furfural is a green key compound which has been identified as of the 30 high value bio-based chemical by US Department of Energy [1]. About 450,000 t of furfural are produced annually from carbohydrates with a major production capacity in China. It can be employed in a wide scale of applications such as oil refining, plastics, pharmaceutics and agrochemicals industries [2]. Furfural itself can be used as a selective solvent for refining of lubricating oils and diesels fuels or serves as chemical feedstock. By transformation, furfural leads to many furan derivatives of great interest (furfuryl alcohol, levulinic acid, furoic acid, furfuryl amine, 5-HMF...) through simple reactions [3–9].

Furfural can be obtained from lignocellulosic biomass, for example agriculture wastes (corncobs, oats, wheatbran...). Lignocellulosic biomass is abundant, cheap, renewable and ideal to replace fossil based products. Nowadays, development of new effective access methods for biomass valorization represents a challenge. Furfural process from raw materials involves a two- step reaction mechanism under acidic conditions: first, depolymerization of pentose-rich lignocellulosic materials to monosaccharides, mainly *D*-xylose then, secondly, dehydration of *D*-xylose to furfural.

Dehydration of *D*-xylose was widely described in literature and usually involves acidic conditions. Many researches mention inorganic mineral acids such as H_2SO_4, HCl, H_3PO_4 [10–13], but also heterogeneous catalysts zeolite, heteropolyacids [14–15]. Solids catalysts are limited by their cost and synthesis, and can be subject to deactivation due to the deposit of by-products on their surface. Main homogeneous catalytic productions have for inconvenient the use of an high pressure, of a corrosive acidic stream which needs to be neutralized, and leads to an high energy comsuption, and fume pollution. One potent way is to develop an eco-friendly and environmentally viable process to access furfural using an alternative to corrosive mineral acids.

In this context, dehydration of furfural was often performed in water thanks to its polarity, safety, sustainability and lower price. As the best of our knowledge, inorganic salts are relatively less used alone for the dehydration of *D*-xylose. Among homogeneous catalysts applied for dehydration of *D*-xylose in water, inorganic salts particularly metal chlorides have shown a beneficial effect on the conversion of *D*-xylose to furfural. Wang et al. [16] showed that $SnCl_4$ as a catalyst in water led to a furfural yield of 63% from *D*-xylose at 130 °C for 6 h. Moreover, they have the advantage to be less corrosive than mineral acids such as H_2SO_4. Particularly, trivalent metal chlorides such as $AlCl_3$ exhibit superior catalytic effect on furfural production and biomass pre-treatment [17–19]. $FeCl_3$ was recently used successfully in the dehydration of *D*-xylose [20]. On the other hand, many by-products have been formed in water

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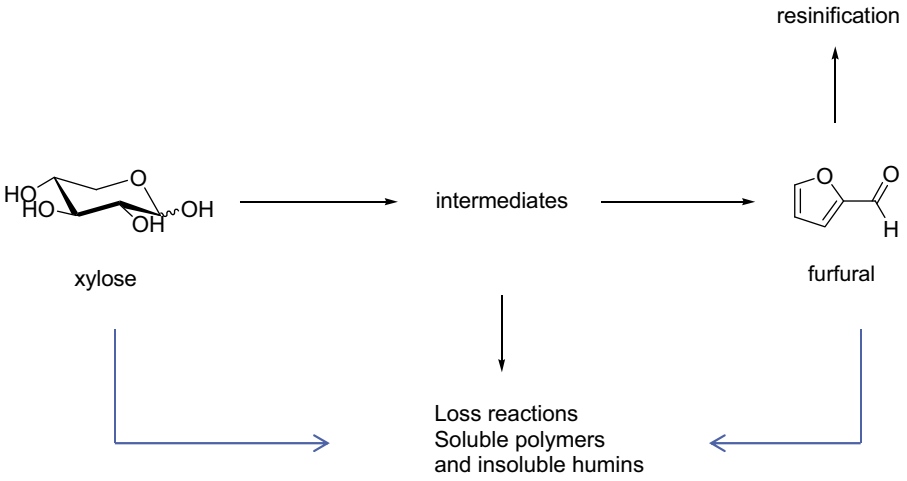

Scheme 1. Simplified reaction pathway for the dehydration of D-xylose to furfural.

condition, therefore leading to a lower selectivity and furfural yield. Undesired side reactions include condensation reactions between furfural and intermediates of *D*-xylose-to-furfural (cross polymerization), reactions of furfural with itself (self polymerization or resinification), as well as degradation of pentoses to low molecular weight products (organic acids, aldehydes) (Scheme 1). These reactions in water generate several side-products, both soluble and insoluble (black carbonaceous compounds also called humins).

To inhibit formation of side products, one of the most promising approaches is to add an organic co-solvent. Using a co-solvent allows the extraction of furfural from the aqueous phase into the organic phase and also improves furfural yield. According to Weingarten et al. [21], a biphasic system does not alter the fundamental kinetics of its entire reaction compared to classic monophasic system. Its only role is to be a storage for the hydrophobic species especially for temperatures under 180 °C. Publications reported often the use of MIBK, toluene, nitrotoluene or dichloromethane as efficient co-solvents [22–25] for the dehydration of *D*-xylose. Stein et al. [20] obtained furfural in a 71% yield at 140 °C using a combination of $FeCl_3$/NaCl in a biphasic system (water/2-MeTHF) under conventional heating. Recently, Campos Molina et al. [26] worked on dehydration of *D*-xylose in water/CPME. Cyclopentyl methyl ether (CPME), considered as green solvent, has been shown to inhibit the generation of undesired products (resins, condensation products and humins). Moreover, CPME gave 100% furfural yield at 170 °C using H_2SO_4. To date, no study about dehydration of *D*-xylose using a biphasic system (water/CPME) under microwave irradiation has been reported in literature.

Microwave-assisted reaction has increased over the last years to become very popular and useful technology in the world. Microwave has many advantages like shorter reaction times, more efficient reactions (higher yields and selectivities) and usuallyless by-products especially in neat conditions. It has been shown that microwave heating may increase yield of dehydration products from carbohydrates [21,27–32]. Recent studies have investigated production of furfural from *D*-xylose and xylan under microwave irradiation. Yemis et al. [33] studied the conversion of *D*-xylose and xylan to furfural using HCl under microwave irradiation. They obtained 59% of furfural from *D*-xylose and 54% from xylan. Yang et al. [34] obtained furfural from *D*-xylose or xylan in monophasic H_2O/THF medium with $AlCl_3$ and NaCl in 75% at 140 °C for 45 min. Weingarten et al. [21] used a water/MIBK system with HCl as catalyst at 170 °C to give 80% of furfural.

In this work, we studied the dehydration of *D*-xylose to furfural in a biphasic system (water/CPME) in presence of inorganic salts under microwave irradiation. Several parameters such as temperature, time, *D*-xylose loading and influence of NaCl addition have been discussed. Later the best conditions were employed to proceed to dehydration of *L*-arabinose, a second pentose derived from biomass and for realizing the direct transformation of xylan.

2. Materials and methods

2.1. Materials

Substrates were purchased from Sigma–Aldrich (*D*-xylose ≥ 99%, xylan from beechwood ≥90%) and from Acros (*L*-arabinose ≥ 99%). Catalysts ($FeCl_3$, $CuCl_2$, $CoCl_2$, $ZnCl_2$, $FeCl_2$, $AlCl_3$, $CrCl_3$, $FeSO_4$ and $Fe(SO_4)_3$) were purchased from Acros. $FeCl_3$ was anhydrous 98%. Hydrochloric acid (37%) and NaCl were obtained from Carlo Erba. Solvents were purchased from Acros (cyclopentyl methyl ether) and Fisher Scientific (acetonitrile). Standard (furfural 99%) was obtained from Acros. All materials were used without further purification. Distilled H_2O was used for preparation of all aqueous solutions.

2.2. General procedure for the synthesis of furfural in water-CPME as biphasic media from D-xylose

In a typical experiment, a 10 mL glass vessel was charged with water (1 mL), CPME (3 mL), *D*-xylose (187.5 mg, 1.25 mmol) and a catalyst (20 mol%). In some experiments, NaCl was also added to the vial (from 0.62 to 2.5 mmol). The vessel was sealed with a septum, placed in the microwave apparatus (AntonPaar Monowave 300) and heated to the desired temperature under magnetic stirring (600 rpm) for the desired time. Temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to 40 °C using compressed air. Then, the two phases were separated. The aqueous phase was diluted in 200 mL of distilled water and filtered prior to analysis through a filter paper (10–20 μm, VWR). The organic phase was diluted in 200 mL of acetonitrile and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR).

2.3. General procedure for the synthesis of furfural in water-CPME as biphasic media from L-arabinose

In a typical experiment, a 10 mL glass vessel was charged with water (1 mL), CPME (3 mL), *L*-arabinose (187.5 mg, 1.25 mmol),