



Cyclopentyl methyl ether: A green co-solvent for the selective dehydration of lignocellulosic pentoses to furfural

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HIGHLIGHTS

- First report on the CPME utilization for furfural production from lignocellulose.
- CPME is a green solvent, in contrast to other tested solvents.
- Study conducted on cardoon biomass, a plant adapted to Mediterranean climates.
- Yields close to 100% can be achieved by using the biphasic CPME/water system.

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ABSTRACT

The effects of cyclopentyl methyl ether (CPME) addition during the aqueous xylose dehydration reaction to furfural are reported here. These investigations were conducted by using pure xylose and *Cynara cardunculus* (cardoon) lignocellulose as sugar source and H_2SO_4 as catalyst. The research was also applied to aqueous solutions containing NaCl, since it has been previously demonstrated that NaCl incorporation to these reaction mixtures remarkably increases the furfural formation rate. It has been found that CPME incorporation inhibits the formation of undesired products (resins, condensation products and humins). Thus, cardoon lignocellulosic pentoses were selectively transformed into furfural (near 100%) at the following reaction conditions: 1 wt.% H_2SO_4 , 4 wt.% biomass referred to aqueous solution, 30 min reaction, 443 K, CPME/aqueous phase mass ratio equals to 2.33, and NaCl/aqueous solution mass ratio of 0.4. In contrast, no effect was observed for cellulosic glucose transformation into hydroxymethylfurfural and levulinic acid at identical reaction conditions.

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1. Introduction

Furfural constitutes a platform compound that can be converted into a wide range of industrially important chemicals. It is a versatile precursor to obtain a wide variety of chemical products through relatively simple reactions (more than 50 have been described in the literature) (Kamm et al., 2006; Alonso-Fagúndez et al., in press; Sádaba et al., 2011). Nowadays, furfural is industrially produced from pentoses (xylose and arabinose) contained in lignocellulosic biomass by a cyclodehydration reaction catalyzed by acids (Karinen et al., 2011; Zeitsch, 2000). D-xylose is the more abundant pentose in most of lignocellulosic feedstocks (Mamman et al., 2008). The industrial process makes use of aqueous solutions of mineral acids as catalysts, typically H_2SO_4 . The overall reaction involves the hydrolysis of pentosan into pentoses (mostly xylose)

and the successive (much slower) dehydration of the latter to form furfural (Dias et al., 2005; Shi et al., 2011).

During the xylose cyclodehydration reaction other non selective processes can take place, thus lowering the potential yield to the desired product (furfural). These side reactions include the condensation of furfural with intermediates of the pentose-to-furfural conversion (to give acetals and hemiacetals, and with derived oligomers (humins)), resinification reactions of furfural with itself producing oligomers and polymers (Zeitsch, 2000) (Dee and Bell, 2011), and finally, fragmentation or decomposition reactions of xylose to other compounds such as glyceraldehydes, pyruvaldehydes, glycoaldehydes, acetol and lactic acid (Karinen et al., 2011).

When these loss reactions take place significantly, the pentose molecules are not selectively converted to furfural and the final furfural yield is smaller compared to the theoretical one. (Zeitsch, 2000). Different technological approaches have been proposed to cope with the furfural loss reactions such as SUPRATHERM and SUPRAYIELD processes (Zeitsch, 2000). Besides, very recently, stripping with N_2 under semi-batch conditions has been reported

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