

Production of furan derivatives by dehydration of biomass-derived carbohydrates

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Introduction

We are entering an era of diminishing availability of petrochemical resources to produce the energy and chemical materials needed by society. Abundant biomass resources are a promising alternative for the sustainable supply of valuable intermediates (e.g., alcohols, aldehydes, ketones, carboxylic acids) to the chemical industry for production of drugs and polymeric materials. Furan derivatives, such as furfural and 5-hydroxymethylfurfural (HMF), can be produced from renewable biomass resources by acid-catalyzed dehydration of pentoses and hexoses, respectively. These compounds have been identified as possible sustainable substitutes for petroleum-based building blocks used in the production of plastics and fine chemicals.¹ Previously, the dehydration of hexoses to form HMF has been conducted in water, aprotic organic solvents (dimethylsulfoxide (DMSO)), and biphasic systems (water/methylisobutylketone (MIBK)) using an array of catalysts, including mineral and organic acids, zeolites, solid acids, and ion exchange resins.² However, these processes either require energy-intensive separation procedures or lead to low product yields.

We present here a catalytic process for the conversion of fructose to HMF using a biphasic reactor containing a reactive aqueous phase and an organic extracting phase (MIBK), chemically modified by DMSO, polyvinylpyrrolidone (PVP), and 2-butanol promoters and using HCl as the acid catalyst. This process produces HMF in high yields, in high concentrations, and delivers it in a separation-friendly solvent. In addition, results for the dehydration of other mono- and polysaccharides, as well as results for the use of niobium phosphate as a high-temperature heterogeneous catalyst are reported.³

Materials and Methods

Aqueous- and organic-phase components were obtained from Sigma-Aldrich Corp. Dehydration experiments were carried out in 10 ml (Alltech), thick-walled glass reactors heated in a temperature controlled oil bath (453 K) placed on a magnetic stirrer. The temperature in the oil bath was controlled using a series 16A temperature controller (Dwyer Instruments) coupled with a 150 W heating cartridge (McMaster Carr). The reaction was stopped by rapidly cooling the reactor in an ethylene glycol bath set at 253 K. Sugar conversion and product selectivity were calculated from the aqueous and organic phase concentrations obtained from HPLC and the corresponding volume of each phase.

Results and Discussion

The effect of aqueous and organic phase promoters on HMF selectivity is shown in Figure 1A. The combination of DMSO and PVP increased the selectivity from 60% to 75%. These promoters increase the rate of fructose conversion into HMF and to some extent decrease the rates of undesirable parallel reactions. The addition of 2-butanol to MIBK as an organic phase promoter improved the partitioning of the HMF product into the organic phase,

thus minimizing degradation reactions arising from extended HMF residence in the reactive aqueous phase and achieving a more efficient recovery of HMF. Starting with a 30 wt% aqueous fructose solution, our results using all 3 modifiers (DMSO, PVP, and 2-butanol) yielded 0.065 g/ml of HMF in the organic layer, with 83% HMF selectivity at 82% conversion. A niobium phosphate solid acid catalyst at 453 K showed promising results of 73% HMF selectivity at 62% conversion.

Preferred reaction conditions for representative monosaccharide units (i.e., fructose, glucose and xylose) were found by adjusting the levels of DMSO, the pH of the solution, and the type of extracting solvent. It was found that the corresponding polysaccharides such as sucrose (a disaccharide of glucose and fructose), inulin (a polyfructan), starch (a polyglucan), cellobiose (a glucose dimer), and xylan (a xylose polysaccharide), can be converted with equally good selectivities at high conversions (Figure 1B). By processing polysaccharides that are inexpensive and abundantly available, the need to obtain monosaccharides in a separate process is eliminated.

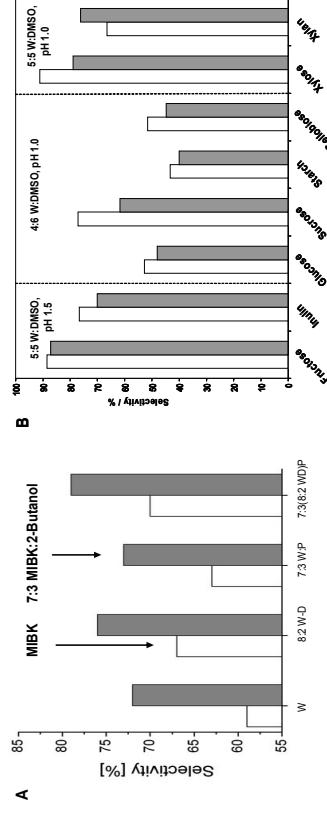


Figure 1. A) Effect of aqueous and organic phase promoters on HMF selectivity. Water (W), DMSO (D), PVP (P). B) HMF and Furfural selectivities for different carbohydrates using 7:3 MIBK-2-butanol (white bars) and dichloromethane (grey bars).

Significance

Furan derivatives, such as HMF and furfural, have been described as key substances that bridge between carbohydrate chemistry and petroleum-based industrial chemistry because of the wide range of chemical intermediates and end-products that can be produced from these compounds for use in the polymer, fuel, and pharmaceutical industries.^{3,4}

References

1. T. Werpy, G. Petersen, *Top Value Added Chemicals From Biomass Available electronically at <http://www.osti.gov/bridge>* (2004).
2. B. M. F. Kuster, *Starch* **42**, 314 (1990)
3. Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science* **312**, 1933 (2006).
4. C. Moreau, M. N. Belgacem, A. Gandmi, *Topics in Catalysis* **27**, 11 (2004).