

Production of HMF from Aqueous Fructose – A Microwave Study

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Introduction and Significance

Today a lot of focus is put on the development of alternatives to the chemical industry based on fossil fuels. The decreasing fossil fuel reserves calls out for a long term and sustainable energy source. This alternative could be provided by carbohydrates in biomass which is abundant in most parts of the world and comes from the light induced fixation of CO₂ in plants and algae. One promising compound that comes directly from the acid catalysed dehydration of hexoses is 5-hydroxymethylfurfural (HMF). This furan-based compound can be utilized as a platform chemical for further processing into commercial valuable chemicals [1] and thereby replace a range of chemicals that are obtained from fossil fuels today (Figure 1).

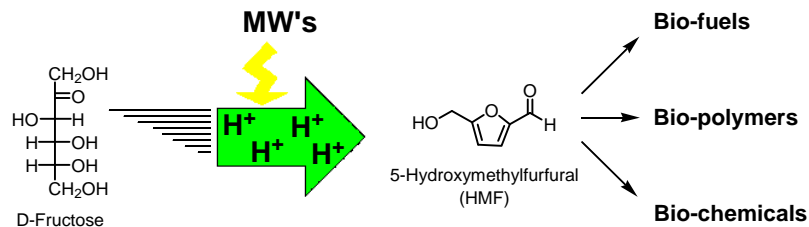


Figure 1. Schematic representation of the green microwave promoted and acid catalyzed dehydration of fructose to HMF.

HMF has been produced mainly from fructose by the means of several acidic catalysts such as mineral acids [2] and acidic resins, [2] and in various solvent systems e.g. water and DMSO [2] and ionic liquids [3]. From an environmental point of view water is the preferred solvent of choice, unfortunately however water is not very selective for the production of HMF and many by-products such as formic acid (FA) and levulinic acid (LA) are produced. Lately microwave induced dehydration of fructose in a water/acetone mixture have proved highly efficient in promoting the synthesis of HMF, thereby greatly reducing the reaction time and increasing selectivities and yields compared with conventional heating [4]. Best results are reported at 150 °C for a water/acetone mixture, but the very high pressure and the resin might be hazardous at these elevated temperatures. Also low fructose concentrations of 2 % along with large amounts of catalyst render this process undesirable from an industrial point of view. In this study we have explored the limits of the microwave induced aqueous dehydration of fructose with respect to yield and selectivity of HMF with HCl as catalyst.

Reaction Procedure

A microwave reactor vessel was charged with an aqueous fructose solution (30 wt. %, 2.7 mL, 5.3 mmol), an aqueous HCl solution (0.1 M, 0.3 mL, 0.03 mmol) and a magnet and subsequently sealed with a cap. The mixture was then mounted in a microwave apparatus (Biotage Emrys Creator, Personal Chemistry, 300 W) and heated for the specified time. The reactor vessel was cooled to room temperature, decapped and a sample was collected and analyzed by HPLC (Agilent 1200 series, Bio-Rad Aminex HPX-87H 300 mm × 7.8 mm pre-packed column, 0.005 M H₂SO₄ mobile phase).

Results and Discussion

Employing an initial high fructose concentration (27 wt. %) exerts a challenge to the process, as polymeric by-products are favored with increasing concentration. However a high fructose concentration is desirable from an industrial point of view, e.g. reducing reactor volume and the amount of solvent needed. This study reveals the temperature (apart from the fructose concentration) to be the single most important parameter in the mild dehydration process, having an optimum at 160 °C for 300 s in water, achieving a selectivity of 59 % at a fructose conversion of 48 % (Figure 2). These results are highly competitive with previous published results for the dehydration in a more advanced water/acetone mixture [4]. In addition, the heating of a 27 wt. % fructose solution in an aqueous 0.01 M HCl solution for only 1 s, increased the HMF selectivity to 63 % at a 52 % fructose conversion.

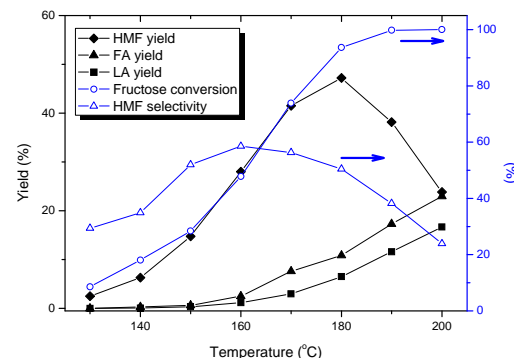


Figure 2. HCl catalyzed dehydration of fructose to HMF as a function of temperature for 300 s and 300 W (♦ HMF yield, ▲ FA yield, ■ LA yield, ○ Fructose conversion and Δ HMF selectivity).

References

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4. Qi, X., Watanabe, M., Aida, T.M., Smith, Jr, R.L., *Green Chem.* 10, 799 (2008).