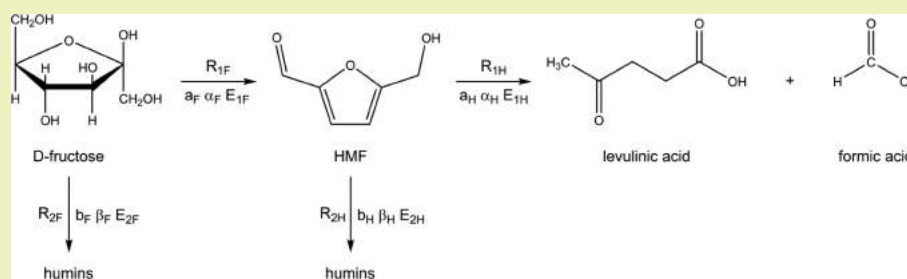


Experimental and Kinetic Modeling Studies on the Sulfuric Acid Catalyzed Conversion of D-Fructose to 5-Hydroxymethylfurfural and Levulinic Acid in Water

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Supporting Information



ABSTRACT: Levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) have been identified as promising biomass-derived platform chemicals. A kinetic study on the conversion of D-fructose to HMF and LA in water using sulfuric acid as the catalyst has been performed in batch setups. The experiments were carried out in a temperature window of 140–180 °C, using sulfuric acid as the catalyst (0.005–1 M) and an initial D-fructose concentration between 0.1 and 1 M. A kinetic model for the conversion of D-fructose to HMF and the subsequent reaction of HMF to LA was developed including the kinetics for the formation of solid byproducts (humins) using a power-law approach. According to the model, the maximum attainable HMF yield in the experimental window is 56 mol % ($C_{\text{fruc}} = 0.1 \text{ M}$; $C_{\text{acid}} = 0.005 \text{ M}$; 166 °C), which is close to the highest experimental value within the range (53 mol %) and considerably higher than that reported for D-glucose. The highest modeled LA yield was 70 mol % ($C_{\text{fruc}} = 0.1 \text{ M}$; $C_{\text{acid}} = 1 \text{ M}$; 140 °C), close to the experimental value of 74 mol %. This LA yield is considerably higher than that found for D-glucose within the range of experimental conditions. The model was used to determine the optimum reactor configuration for highest HMF and LA yields, and it is shown that highest HMF yields are attainable in a PFR reactor, whereas a large extent of backmixing is favorable when aiming for a high LA yield.

KEYWORDS: D-Fructose, HMF, Levulinic acid, Kinetic modeling

INTRODUCTION

The steady growth of the use of fossil resources has led to higher prices for fossil energy, fuels and petrochemical products as well as environmental concerns related to CO₂ emissions. As a result, the use of renewables is receiving high attention.^{1–10} Biomass is considered a very attractive renewable source for the production of bioenergy, biofuels and biobased chemicals. Biomass is produced at an estimated rate of 170 billion metric tons per year by photosynthesis, though only 3–4% is used by humans for food- and nonfood applications.^{11–14}

Lignocellulosic biomass is an interesting source for five-carbon sugars (D-xylose and L-arabinose) and six-carbon sugars (like D-glucose, D-mannose, D-fructose, and D-galactose) that can be converted into several interesting platform chemicals.^{2,11,13} 5-Hydroxymethylfurfural (HMF) and levulinic acid (LA) have been identified as very attractive platform chemicals derived from C6 sugars. Both HMF and LA may be converted to a wide range

of derivatives with a broad application range (Figure S1, Supporting Information).^{2,3,10,15,16}

HMF and LA are accessible from the C6 sugars in lignocellulosic biomass by an acid-catalyzed dehydration process. In the first step, the hexoses are dehydrated to HMF, which may react further to form LA together with formic acid (FA). The simplified reaction scheme is depicted in Scheme 1.

A wide range of catalysts (both homogeneous and heterogeneous), solvents, and solvent combinations have been explored and reviewed.^{5–7,17,18} As part of a larger program to determine the kinetics of the individual steps in the conversion of C6 sugars to HMF/LA to be used as input for the development of efficient reactor configurations, we here report a kinetic study

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