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Experimental and modeling studies on the acid-catalyzed conversion of inulin to 5-hydroxymethylfurfural in water

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ABSTRACT

Inulin is considered as an attractive feed for the synthesis of 5-hydroxymethylfurfural (HMF), an important biobased platform chemical with high application potential. We here report a systematic study to optimize the HMF yield from inulin in a batch reactor for reactions in water using sulphuric acid as the catalyst. The latter was selected on the basis of a screening study with seven organic- and inorganic Brönsted acids (H_2SO_4, HNO_3, H_3PO_4, HCl, trifluoroacetic acid, maleic acid and fumaric acid). The effect of process conditions such as temperature (160–184 °C), inulin loading (0.05–0.17 g/mL), sulphuric acid concentration (0.001–0.01 M) and reaction time (0–60 min) on HMF and levulinic acid (LA) yields were determined experimentally and subsequently modeled using non-linear multivariable regression. The highest experimental HMF yield was 39.5 wt% (50.6 mol%) and was obtained at 170 °C, an inulin loading of 0.17 g/mL, a sulphuric acid concentration of 0.006 M and a reaction time of 20 min. Agreement between experiments and model for both HMF and LA yield was very satisfactorily.

1. Introduction

Biomass is a renewable source for bioenergy, biofuels and biobased chemicals and has attracted high interest in recent years (Hoogwijk et al., 2005; Demirbas, 2009; van Putten et al., 2013; Sheldon, 2014; Delidovich et al., 2014; Agirrezabal-Telleria et al., 2014). For instance, biofuels have been commercialized (bioethanol from sugars, biodiesel from plan oils) and are available on the market. However, substantial research and development activities will be required to develop and commercialize efficient chemical processes for the production of a wide range of biobased chemicals. Bozell and Petersen (2010) compiled a list of 12 biobased chemicals that have highest techno-economical potential (Werpy and Petersen, 2004). The top 12 list includes 5-hydroxymethylfurfural (HMF), which may be converted to versatile building blocks for polymers such as 1,6-hexanediol (Buntara et al., 2012), 2,5-furandicarboxylic acid (Boisen et al., 2009) and fuel-additives such as 2,5-dimethylfuran (Roman-Leshkov et al., 2007).

HMF is typically obtained by reacting C6 sugars in water in the presence of a Brönsted acid (Barrett et al., 2006; Bicker et al., 2003; Huber and Dumesic, 2006; Corma et al., 2007; Hu et al., 2008; Tong et al., 2010; Amiri et al., 2010; van Putten et al., 2013; Choudhary et al., 2013; Agirrezabal-Telleria et al., 2014; Wang et al., 2014). By-products of the reaction are levulinic acid and formic acid (Girisuta et al., 2008) and insolubles known as humins (van Zandvoort et al., 2013). In water, fructose gives a maximum HMF yield of around 55 mol%, whereas the yields for glucose are less than 10 mol%. Higher HMF yields from

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