



Production of 5-hydroxymethylfurfural and furfural from a mixed saccharide feedstock in biphasic solvent systems

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ABSTRACT

The industrial platform chemicals 5-hydroxymethylfurfural (HMF) and furfural (FF) were produced from mixed mono- and oligosaccharides in a hydrolysate obtained from the prehydrolysis of radiata pine wood chips. The conversions were performed at high temperatures in an autoclave using either a THF/water biphasic system under both Brønsted and Lewis acid catalysis provided by $\text{NaHSO}_4/\text{ZnSO}_4$, or an acetone/water biphasic system under Brønsted acid catalysis afforded by H_3PO_4 . Treatment in a THF/water system at 160 °C for 90 min gave the highest yields of HMF (40 molar%) and FF (58 molar%), while the best conditions for the acetone-water system were 180 °C/80 min for HMF (36 molar%) and 170 °C/30 min for FF (62% molar%). Yields for HMF and FF were based on respective hexose and pentose saccharide contents of the solids. The results show that mixed saccharide by-products of thermo-mechanical pulping can be converted into furans at moderately high yields by both catalytic systems.

1. Introduction

The quest for bio-based alternatives for chemicals and materials derived from non-renewable resources has been gaining momentum in recent years, as seen in the amount of research related to lignocellulosic biomass biorefineries (Dessbesell et al., 2017; Liu et al., 2012; Rosatella et al., 2011). Fermentation of naturally-occurring sugars and hydrolysed oligo- and polysaccharides to bioethanol is a well-known biorefinery application. These saccharides can also be reacted to generate biochemicals of higher value than ethanol (Liu et al., 2012; Mamman et al., 2008; Reyes et al., 2013). These include 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), which are liquid biofuels of higher fuel value than ethanol, and building blocks of bio-based plastics, foams, textiles, resins and adhesives such as 2,5-furandicarboxylic acid (FDCA), adipic acid and furfuryl alcohol (Mamman et al., 2008; Rosatella et al., 2011; Teong et al., 2014). As direct conversion to final products is usually not possible or economically feasible, a commonly employed strategy is to look for efficient ways to convert biomass saccharides into the versatile chemical intermediates 5-hydroxymethylfurfural (HMF) and furfural (FF). These intermediates can then be efficiently converted to a variety of final bioproducts (Dessbesell et al., 2017; Liu et al., 2012; Rosatella et al., 2011; Teong et al., 2014; Yang et al., 2012). Industrial production of FF involves acid-catalysed hydrolysis of aldoses from agricultural and forest industry by-products. In 2008, the annual production of FF was quoted as 250,000 t (Mamman et al., 2008). The worldwide

production of HMF from biomass is low due to challenges relating to its isolation and purification from the reaction mixtures (Teong et al., 2014).

Conversions of biomass saccharides to biochemicals typically give rise to complex mixtures of products whose composition depends on reaction conditions such as temperature and acidity of the reaction medium and the presence or absence of added catalysts. Aldohexoses such as glucose are readily dehydrated to yield HMF under acidic conditions and high temperatures (Rosatella et al., 2011), while the analogous dehydration of aldopentoses such as xylose produces FF (Rasmussen et al., 2014; Yang et al., 2012). These and other aldoses may be directly dehydrated to HMF and FF or the conversions may proceed via the corresponding ketosugars such as fructose and xylulose (Rasmussen et al., 2014). In addition, HMF, FF and aldoses may react by condensation to produce humins (insoluble polymers of furans and aldoses) (Hu et al., 2012; Rasmussen et al., 2014; Van Zandvoort et al., 2013; Zhuang et al., 2017) that currently have no industrial applications. HMF can also be rehydrated to yield levulinic acid (also a platform biochemical) and formic acid (Rackemann and Doherty, 2011; Rasmussen et al., 2014). These different pathways are illustrated in Fig. 1.

As yields of HMF and FF from simple Brønsted or Lewis acid-catalysed single-phase conversions of carbohydrates in water or organic solvent are generally low (Cai et al., 2014; é et al., 2002; Wei and Wu, 2017), different catalysts and solvents such as ionic liquids with metal

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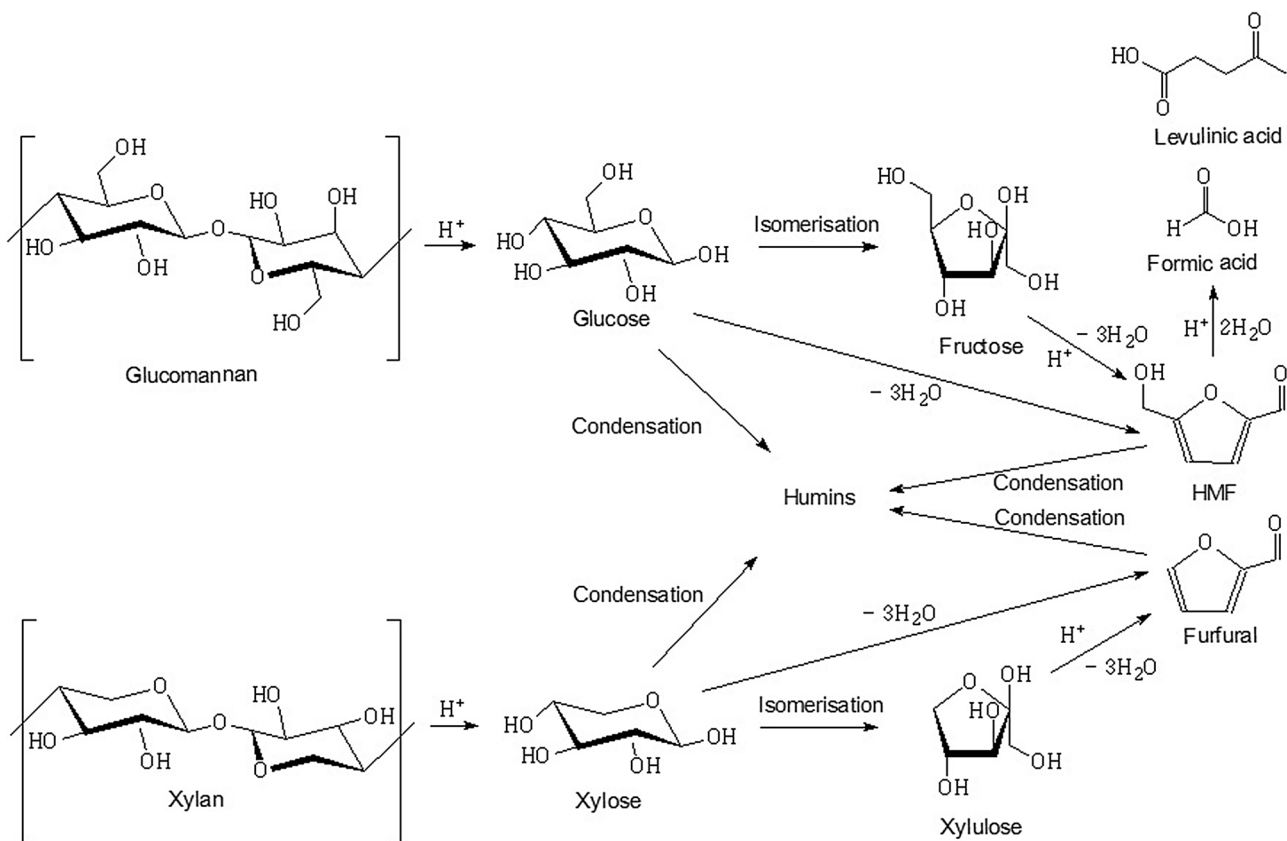


Fig. 1. Pathways in the conversion of woody oligo- and polysaccharides to HMF, FF, humins and organic acids. The mannose formed from glucomannan is expected to behave similarly to glucose but the relative rates of the different pathways may differ.

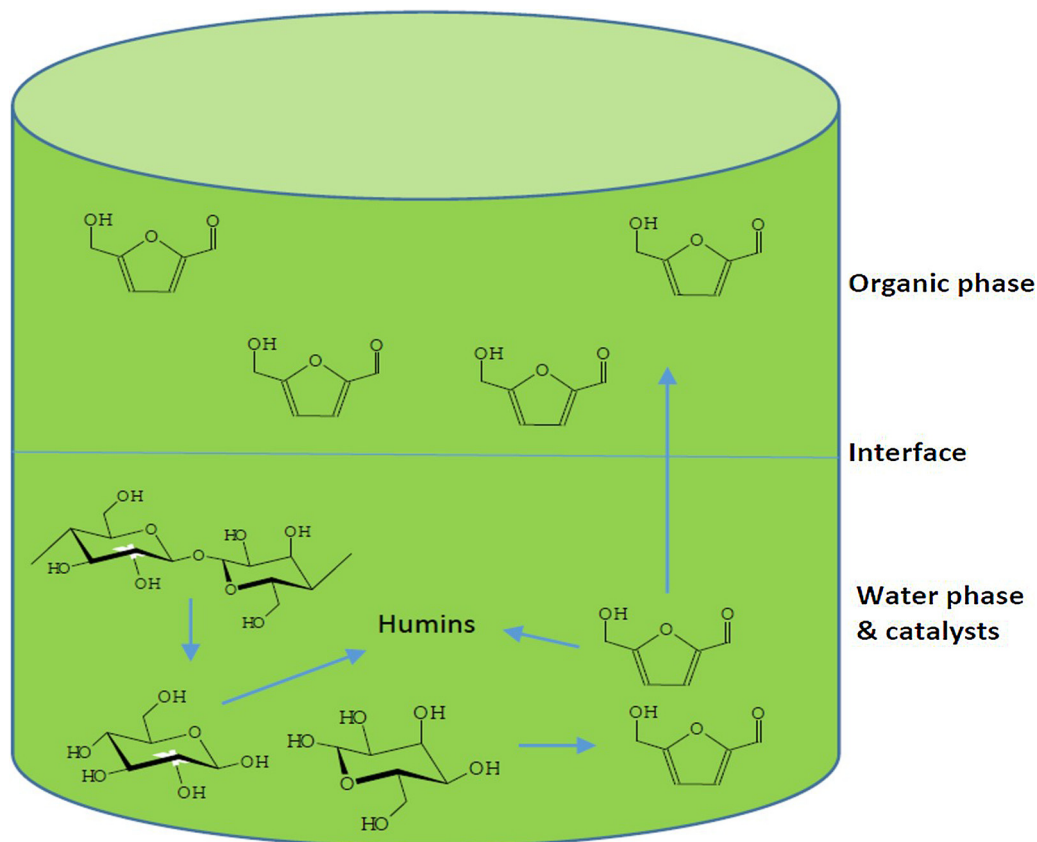


Fig. 2. An example of a catalytic biphasic system for converting oligosaccharides into furans, demonstrated for hexoses. Pentoses undergo a similar conversion.

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