Acid-catalyzed conversion of mono- and poly-sugars into platform chemicals: Effects of molecular structure of sugar substrate

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HIGHLIGHTS

► Molecular structures determine reaction pathways of sugars during acid-treatments.
► Levulinic acid/ester yields: fructose > glucose > galactose ∼ levoglucosan.
► Reaction pathways for soluble polymer from fructose and glucose are different.
► Behaviors of poly-sugars were largely determined by their basic units.
► Steric hindrance negatively affects access of poly-sugars to catalytic sites.

GRAPHICAL ABSTRACT
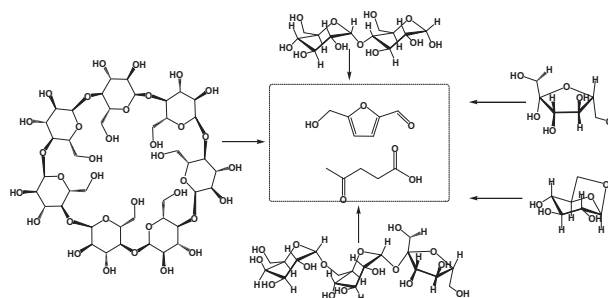
Although both the mono-sugars and poly-sugars could be converted into 5-(hydroxymethyl)furfural (HMF) and levulinic acid, the yields are quite different due to their unique molecular structures.

ARTICLE INFO

ABSTRACT

Hydrolysis/pyrolysis of lignocellulosic biomass always produces a mixture of sugars with distinct structures as intermediates or products. This study tried to elucidate the effects of molecular structure of sugars on their acid-catalyzed conversions in ethanol/water. Location of carbonyl group in sugars (fructose versus glucose) and steric configuration of hydroxyl groups (glucose versus galactose) significantly affected yields of levulinic acid/ester (fructose > glucose > galactose). The dehydration of fructose to 5-(hydroxymethyl)furfural produces much less soluble polymer than that from glucose and galactose, which results in high yields of levulinic acid/ester from fructose. Anhydrate sugar such as levoglucosan tends to undergo the undesirable decomposition to form less levulinic acid/ester. Catalytic behaviors of the poly-sugars (sucrose, maltose, raffinose, β-cyclodextrins) were determined much by their basic units. However, their big molecular sizes create the steric hindrance that significantly affects their followed conversion over solid acid catalyst.

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1. Introduction

5-(Hydroxymethyl)furfural (HMF) and levulinic acid/esters are building blocks for chemical diversity due to their tunable functional groups (Huang et al., 2012; Zhang and Zhao, 2010; Lin and Huber, 2009). Their production from renewable resources has attracted great interests with an aim to reduce the reliance on fossil fuels (Alonso et al., 2010; Yemis and Mazza, 2012; Wang et al., 2011; Sun et al., 2011; Climent et al., 2011; Qi et al., 2009; Yang et al., 2012). The mono-sugars such as fructose can be an ideal precursor for HMF production (Román-Leshkov et al., 2006; Qi et al., 2008; Asghari and Yoshida, 2006). Nevertheless, there is a real concern about its possible competition for food supply. It has become increasingly important to explore new routes for the production of platform chemicals from non-edible biomass.

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Hydrolysis or pyrolysis of lignocellulosic biomass have been widely performed to produce the chemicals or fuels (Benoit et al., 2010; Lange et al., 2010; Binder and Raines, 2009; Gallezot, 2008; Du et al., 2011; Deng et al., 2009).

During the acid-treatment or thermal treatment, the macro structures of biomass are disintegrated, producing a mixture of mono-sugars, sugar oligomers and anhydrosugars (Mourant et al., 2011). These sugars differ in size (sugar oligomer versus mono-sugar) and steric configuration (glucose versus levoglucosan, fructose, galactose and etc.) (Mohan et al., 2006). Thus, several basic but very important questions must be answered to realize the acid-catalyzed conversion of the sugar mixtures. For example, what are the effects of the molecular structures on their reactivities to HMF or levulinic acid? Moreover, polymerization is one of the main challenges in the acid-catalyzed conversion of sugars (Chuntanapum and Matsumura, 2009). Hence, what are the relationship between the molecular structure of a sugar and its propensity to polymerize? Sugar oligomers are characterized by the presence of glycosidic bonds to connect the sugar monomers. These oligomers are the intermediates during the hydrolysis/pyrolysis of biomass; for example, they are abundant in bio-oil (Huber et al., 2006; Gunawan et al., 2012; Garcia-Perez et al., 2008; Bennetta et al., 2009). What are the differences between sugar oligomers and mono-sugars in terms of their reactivity when subject to a solid acid catalyst? How does the glycosidic bond affect the reactivity of sugar oligomers? Although the acid-catalyzed conversion of various sugars such as levoglucosan (Bennetta et al., 2009; Hu and Li, 2011; Gunawan et al., 2012), glucose (Zhao et al., 2007; Hu et al., 2011) and other sugars (Dong et al., 2009; Hu et al., 2012a) have been widely performed, a comprehensive study of the catalytic behaviors of these different sugars at the same conditions is necessary to answer the questions raised above.

This study focused on the acid-catalyzed conversion of mono-sugars (fructose, glucose, levoglucosan, galactose), poly-sugars (sucrose, maltose, raffinose, β-cyclodextrins) and cellulose in ethanol/water over a solid acid catalyst, Amberlyst 70. Their reactivities to form HMF, ethyl levulinate (a fuel and fragrance additive) (Lange et al., 2010), levulinic acid and their tendencies to form soluble and insoluble polymers are related to their molecular structures.

2. Methods

2.1. Materials

The chemicals used in this study were analytic grade and obtained from Sigma–Aldrich, Merck Australia, LC Scientific Inc. (Canada), and Carbosynth Limited (U.K.). Amberlyst 70, a commercially available solid acid catalyst, was used directly without further treatment. The stability of the catalyst under the experimental conditions was investigated in the conversion of levoglucosan in water. The results, which are based on the yields of levulinic acid, show that the catalyst maintained ca. 70–80% of its initial activity after two cycles.

2.2. Experimental procedure

A 130 mL Hastalloy batch autoclave reactor (Autoclave Engineers) was used to perform the sugar conversion reactions. Sugar and Amberlyst 70 (sugar loading: 13 wt.%; catalyst loading 15 wt.%) was mixed with ethanol/water (ethanol/water molar ratio: 0.5:1; total weight: 92.5 g) and loaded into the reactor at room temperature (28 °C). The reaction mixtures were firstly stirred with a stirring rate of 500 rpm at the room temperature for 15 min, and then were heated up to 175 °C in 20 min. The

sample was taken at a 20 min interval and the reaction temperature was maintained at 175 °C for 120 min. After cooling down of the reactor, the residual solution together with the catalyst was collected and separated via filtration. Catalyst and the solid particles were dried in oven at 105 °C for 4 h to constant weight to measure the formation of the solid polymers.

2.3. Analytical methods

The products were measured with an Agilent GC/MS (6890 series GC with a 5973 MS detector) with a capillary column (HP-INNOWax). The injection port was maintained at 250 °C, while the temperature of the column was maintained initially at 35 °C and then to 260 °C at a heating rate of 10 °C min⁻¹. Helium (2.0 mL min⁻¹) was used as the carrier gas. The samples were diluted in acetone to a concentration of ca. 10 wt.% and then directly injected into GC/MS. The compounds were identified with the GC/MS library (NIST MS Search 2005) and were further confirmed with injection of standards if available. In order to quantify the compounds of interest, calibration curves were obtained by injecting standard solutions to calculate concentrations of the compounds. As for the compounds without standards available, the signal intensity (peak area) was used to measure the abundance changes of the compounds without standards.

A derivatisation method was used to determine concentrations of the mono-sugars, broadly following the procedures in the literature (Chen and Mcginnis, 1981). The derivatisation products from the poly-sugars were too heavy to be detected by GC/MS. However, the poly-sugars used in the study decomposed easily to glucose in the presence of acid catalyst. Thus, the concentration of glucose can be used as one of the reference for the concentration of the poly-sugars in solution.

The FT-IR spectra of the catalyst together with the insoluble polymers were characterized with a Perkin-Elmer Spectrum GX FT-IR/Raman Spectrometer with a spectral resolution of 4 cm⁻¹. The spectrum represents the average of 10 scans. The UV-fluorescence spectra of the soluble polymers were recorded using a Perkin-Elmer LS50B spectrometer. The synchronous spectra were recorded using a constant energy difference of −2800 cm⁻¹ with the scan speed was 200 nm/min. The concentration of the samples was diluted to with methanol to 40 ppm, which is in the linear range of response of the UV-fluorescence spectra to the concentrations of the soluble polymer.

Definition of sugar conversion is as follows:

Conversion(mol%)

$= (1 - \text{moles of sugars in product/moles of the sugars loaded})\%$

Yields of products are defined by the formula:

Yields(mol%)

$= (\text{Moles of the compound in products/}$

Theoretical moles of the compound from the sugar loaded)

$\times 100\%$

3. Results and discussion

3.1. Catalytic behaviors of the mono-sugars

Fig. 1 shows the conversion of mono-sugars and their product distribution as a function of reaction time. The dehydration of fructose to HMF even started at room temperature in the presence of the acid catalyst after stirring for 15 min (Fig. 1a and c). Most fructose was converted and HMF was the main initial product with the increase of reaction temperature to 175 °C in 20 min. HMF