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Biomass-derived sugars and furans: Which polymerize more during their hydrolysis?

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ABSTRACT

Sugars and furans are important intermediates during the conversion of non-food lignocellulosic biomass to biofuels and chemicals. In this study, polymerization of the sugars (glucose, fructose, xylose) and furans (5-hydroxymethylfurfural, furfural) during their acid-catalyzed conversion was investigated. The potential cross-polymerization between sugars and furans was explored. Sugars and furans have very different tendencies towards polymerization. Yields of solid polymer (weight basis) during the dehydration of glucose to 5-hydroxymethylfurfural (HMF) is ca. 7% while that from HMF to levulinic acid is ca. 17% at 190 °C with Amberlyst 70 as the catalyst. Dehydration of xylose to furfural forms negligible amounts of solid polymer, while furfural polymerized almost completely. Cross-polymerization between HMF and glucose is insignificant. However, HMF does cross-polymerize with fructose and furfural, producing more insoluble polymer and soluble polymers with different structures. The cross-polymerization between furfural and xylose, if any, does not have any appreciable impact on formation of the insoluble polymer or soluble polymer. Efforts should be devoted more to stabilize the furans to diminish their polymerization during acid-catalyzed conversion of biomass/sugars/furans to value-added chemicals or biofuels.

1. Introduction

Glucose and xylose are the intermediate products during the conversion of lignocellulosic biomass to platform chemicals such as 5-hydroxymethylfurfural (HMF), furfural and levulinic acid [1,2]. In an acidic reaction environment, glucose and xylose not only can dehydrate to the furans (HMF and furfural) [3,4], but also polymerize, reducing process selectivity [5–7]. The polymerization can also deactivate solid acid catalysts and make regeneration of the carbon-based acid catalyst difficult [8]. Polymerization of sugars and furans is a major hurdle for the selective production of chemicals and biofuels from biomass via acid-catalyzed reactions.

Dehydration of sugars initiates from the protonation of their hydroxyl groups, forming reactive intermediates with carbon cations and/or conjugated π bonds [9,10]. These reactive intermediates have many reaction routes to go and polymerization is an important one. Rehydration of the furans like HMF or furfural also leads to the formation of reactive intermediates and the followed polymerization [11–13]. The polymerizations from sugars, furans, and the cross-polymerization between sugars and furans have been illustrated in the schemes in many papers [14–17].

One puzzle, which has not been clarified yet, is the specific contribution of direct sugars polymerization, furans polymerization and their cross-polymerization towards polymer formation. The degradation/polymerization of different sugars and furans proceed via very different ways, and in our previous study we found that the C6 sugars (glucose), C5 sugar (xylose) and the sugar oligomers (raffinose) interact with each other to different extents [15]. However, we have not yet clarified the specific contribution of sugars (glucose, xylose) and their derived furans (HMF, furfural) towards polymerization as well as their potential interactions. Understanding this is essential to optimize the process design in biorefinery to the selectively produce both sugars and furans from biomass.

In this study, a set of experiments were designed to understand the possible cross-polymerization between sugars and furans as well as their specific contribution to formation of the soluble polymers and insoluble polymers. The acid treatment of the single sugar (glucose, fructose, xylose) and furans (HMF, furfural) as well as the mixed HMF/glucose, HMF/fructose, HMF/furfural and furfural/xylose were investigated at 190 °C with Amberlyst 70 as the catalyst. The π-conjugated structures of the soluble polymers were characterized with UV-fluorescence spectroscopy. The functionality of the insoluble polymer was characterized with Fourier Transform infrared spectroscopy (FT-IR).

Our results demonstrate that 1): during dehydration of glucose to HMF, yield of the insoluble polymer (ISP) is ca. 7% while from HMF to levulinic acid (LA) the ISP yield is more than doubled; 2): the cross-polymerization between glucose and HMF is insignificant due to different time frame for their polymerization; 3): the soluble polymer (SP) formed from HMF is different to that from glucose due to the different reactive intermediates involved; 4): HMF cross-polymerizes with fructose and furfural, producing more ISP and the SP with different structures; 5): the cross-polymerization between xylose and furfural is

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insignificant (if any); 6): during the dehydration from xylose to furfural the amount of ISP formed is negligible, while the ISP formed mainly originates from furfural polymerization.

2. Experimental

2.1. Materials

All the regents used in this study are analytical grade. The sugars, furfural and LA were purchased from Sigma-Aldrich. HMF was purchased from Nanjing Zelang Medical Technology Co., Ltd. Amberlyst 70 was purchased from Dow Chemicals (Shanghai). The chemicals and the catalyst were used directly without any further treatment.

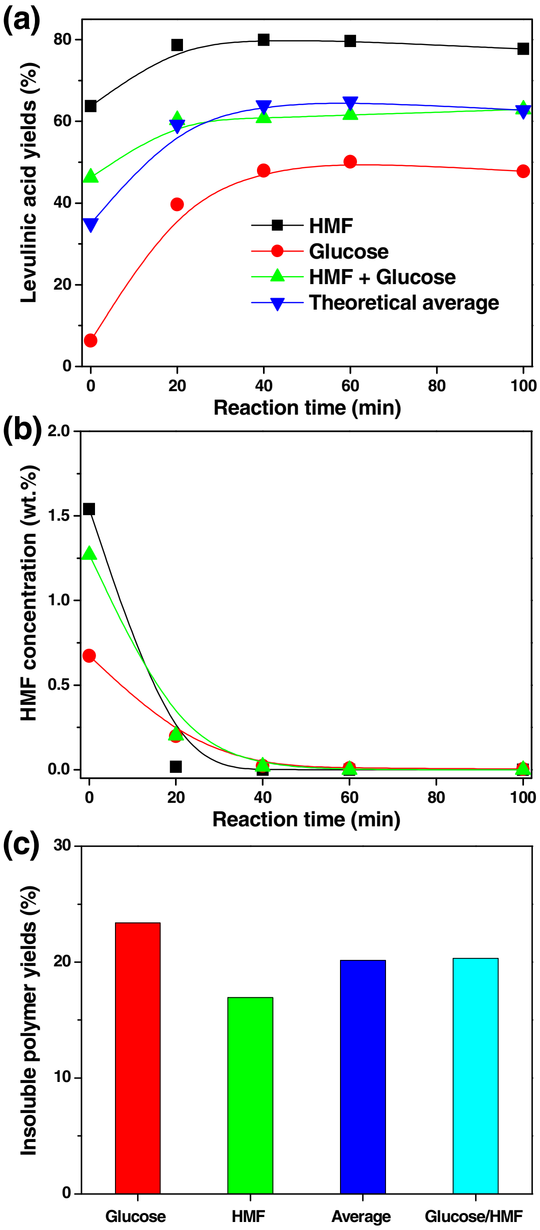

Fig. 1. Products/reactant distributions in acid-catalyzed conversion of glucose, HMF and glucose/HMF. "0 min" in x-axis of a and b means the reaction temperature just reached 190 °C in ca. 12 min. "Theoretical average" in a or the "Average" in c means the average yields (by sum up that from single glucose and single HMF and then divided by 2) of LA or insoluble polymer from acid-treatment of single glucose and single HMF.

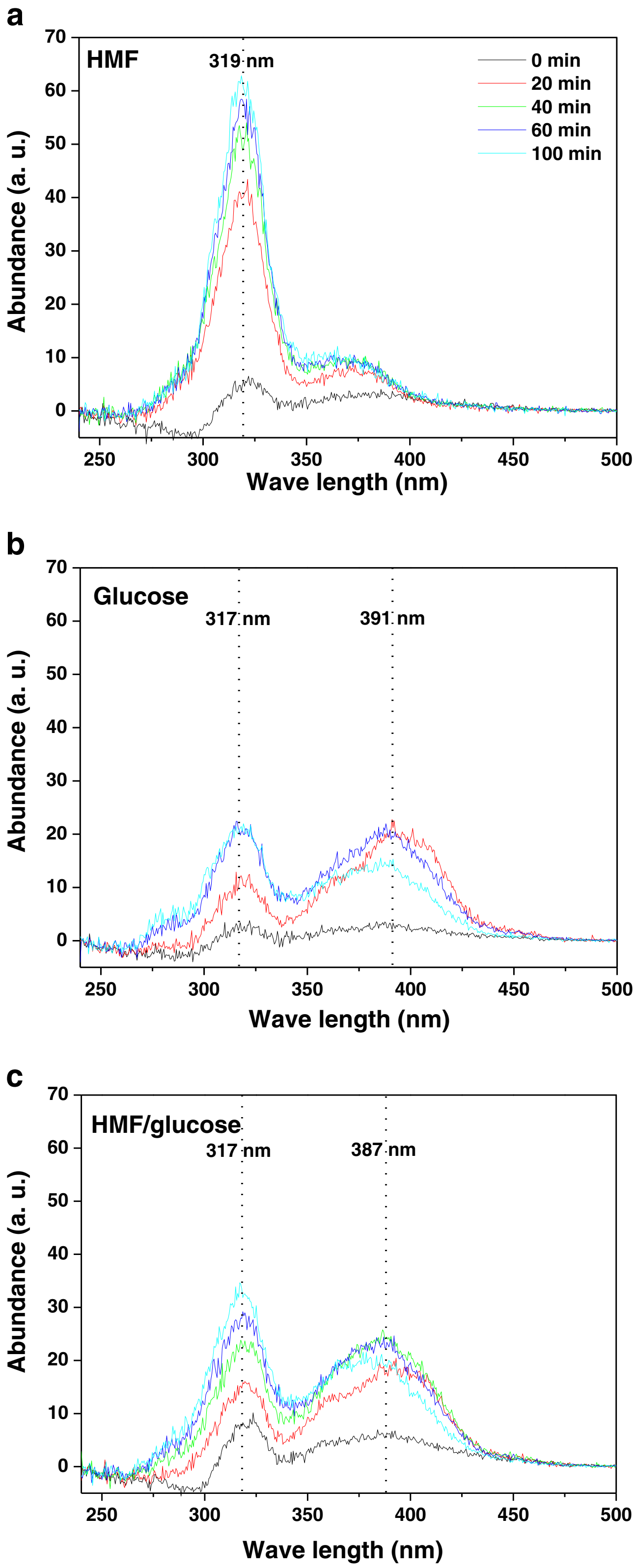

Fig. 2. Constant energy (-2800 cm^{-1}) synchronous spectra for the soluble polymers from the acid-treatment of HMF, glucose and HMF/glucose.

2.2. Experimental procedures

Acid-catalyzed conversion of the sugars and furans were performed in an autoclave (Autoclave Engineers, Division of Snap-Tite Inc.) in an inert atmosphere under the autogenous vapor pressure with a stirring