

Conversion of Fructose into Levulinic Acid by Catalysis of Ionic Liquid

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Abstract—76% Yield of levulinic acid was obtained from fructose conversion catalyzed by acidic ionic liquid in water. The chemical structures and morphologies of humin byproduct were investigated, indicating three stages of transition for the first time. At the early stage, 5-hydroxymethylfurfural (HMF) intermediate from fructose dehydration can take part in humin formation through two sites. When HMF intermediate was completely converted, humins can react further on aldehyde groups, as evidenced by disappearance of 2-formylfuran rings. If the reaction time was long enough, humins can undergo subsequent aromatization, with the furan rings reduced and the C=C groups increased.

Keywords-fructose; levulinic acid; ionic liquid; biomass

I. INTRODUCTION

Due to diminishing fossil resources and increasing concern about sustainable development, biomass conversion to fuels and chemicals has attracted a lot of interests [1]. As one of the identified platform chemicals, levulinic acid (LA) serves as a versatile building block for fuel additives, polymer precursors, herbicides, pharmaceutical, flavour substances and chemical intermediates [2]. Converting monosaccharide biomass of fructose to LA could be regarded as a model at molecular level to understand the reaction mechanism easily. Recently, InCl_3 was used to catalyze the conversion of fructose into LA with a yield of 45% in water [3]. Meanwhile, conversion of fructose to LA catalyzed by H_2SO_4 in γ -valerolactone was reported, leading to ca. 70% yield of LA [4]. During the process of fructose conversion, dark-brown insoluble byproducts, known as humins, are unavoidably formed. Most of the researches in biomass conversion have been focused on the reaction pathway of soluble products such as 5-hydroxymethylfurfural (HMF) and LA, whereas little attention has been paid to the formation and structure of humins. However humins oftentimes compete with desired products, restrain the catalytic activity, and hinder the catalyst reuse and product separation. Thereby elucidation of humins mechanism and inhibition of humins formation will help to improve the efficiency of biomass conversion process.

Several groups have made efforts to understand the mechanism and chemical structure of humins from fructose conversion. For hydrothermal treatment of fructose in the absence of any additional catalysts at 120-140 °C, Yao et al. [5] proposed that fructose first undergoes intramolecular

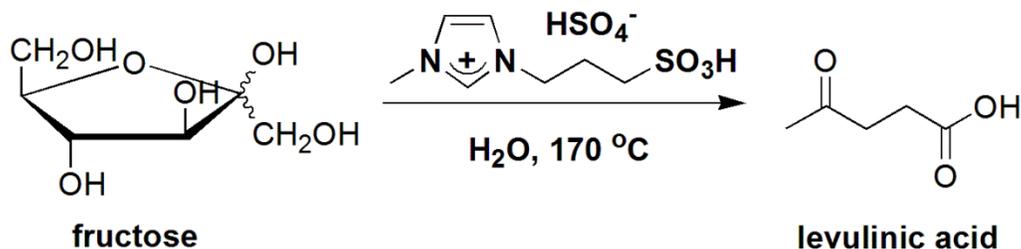
dehydration to HMF, and HMF further polymerizes to form carbon spheres, which contain a dense hydrophobic carbon core and a hydrophilic shell according to field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images. For H_2SO_4 -catalyzed fructose conversion at 135 °C, Patil et al. [6] suggested that fructose must first be converted to 2,5-dioxo-6-hydroxyhexanal (DHH), which subsequently undergoes aldol addition and condensation to form humins. For hexose derived humins catalyzed by H_2SO_4 at higher temperature of 180 °C, van Zandvoort et al. [7] inferred a polyfuranic molecular structure, wherein the inclusion of DHH and limited LA occurs through aldol condensations with the aldehyde groups of HMF or DHH itself.

In our previous work, it was found that SO_3H -functionalized acidic ionic liquids especially 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$), are environmentally friendly catalysts to convert cellulose into LA with high yield and selectivity [8, 9]. Herein, we report on the acidic ionic liquid-catalyzed fructose conversion to platform chemical LA in a yield up to 76% (Scheme 1), whereas chemical structure and morphology of humin byproducts were investigated under the same reaction conditions.

II. EXPERIMENTAL SECTION

D-Fructose (99%) was purchased from Beijing Solarbio Science & Technology Co., Ltd. The ionic liquid 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$) was synthesized by acidification of the zwitterion according to literature [8] and characterized by NMR before use. ^1H NMR (400 MHz, D_2O): δ =8.26 (s, 1H; N-CH-N), 7.05 (s, 1H; CH), 6.99 (s, 1H; CH), 3.89 (t, J =7 Hz, 2H; N-CH₂), 3.43 (s, 3H; N-CH₃), 2.46 (t, J =7 Hz, 2H; CH₂-S), 1.80-1.88 ppm (m, 2H; CH₂); ^{13}C NMR (100 MHz, D_2O): δ =135.6, 123.2, 121.7, 47.2, 46.7, 35.2, 24.5 ppm.

The NMR spectra were recorded on Varian INOVA 400 MHz spectrometer. The infrared spectra were recorded on Bruker Equinox 55 infrared spectrometer. Elemental analyses were determined with the instrument Elementar Vario EL III CHN analyzer. Scanning electron microscopy (SEM) images were acquired on Nova NanoSEM 450 field emission scanning electron microscopy, whereby samples were coated with a thin Aurum film.



Scheme 1. Ionic liquid-catalyzed fructose conversion to levulinic acid (LA)

Fructose (0.925mmol), $[C_3SO_3Hmim]HSO_4$ (1.000g) and de-ionized water (6.000 g) were mixed in a 30mL autoclave with Teflon lining and heated in an oil bath at 170°C for 0, 12, 20, 30, 40, 50, 60, 80 min, 3 h, and 12 h. After reaction, the autoclave was cooled in an ice bath immediately. The crude product was analyzed by 1H NMR using ionic liquid as internal standard. The humin solid was filtered, washed with 15mL of water for three times, dried at 80 °C for at least 24 h and sent to instrumental analysis.

III. RESULTS AND DISCUSSION

During the fructose conversion to LA, HMF was observed as intermediate from intramolecular dehydration of fructose. As shown in Fig. 1, the yield of HMF rose up to 21% with the reaction time increasing from 12 to 20 min, and decreased afterwards, whereas no HMF could be detected in liquid phase after reaction for 50 min. On the other hand, the yield of LA ascended to 71.0% at 50 min, indicating HMF intermediate underwent rehydration to form LA. The yield of LA increased slightly to 76.3% after reaction for 3 h and leveled off, for 76.2% LA yield was obtained after reaction for 12 h.

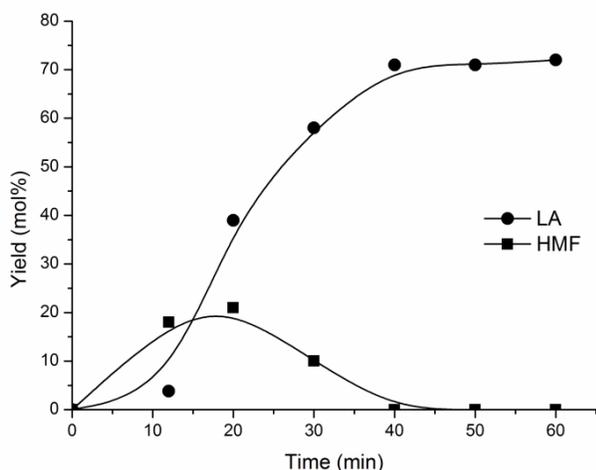


Figure 1. The yield of LA and HMF during fructose conversion
Conditions: 0.925mmol fructose, 1.000 g $[C_3SO_3Hmim]HSO_4$, 6.000 g H_2O , 170 °C

The humin byproducts formed during fructose conversion were investigated by IR spectra (Fig. 2). After

reaction for 12 min, three bands at 1510, 1026 and 804 cm^{-1} were clearly observed, which are characteristic of furan rings vibrations and attributed to C=C stretching vibrations, C-O vibrations of furan rings and aromatic C-H out-of-plane bending vibrations, respectively, indicating HMF could be linked into humin structure through aldehyde group predominantly [6]. Meanwhile, another set of two bands at 1674 and 1591 cm^{-1} were noticeable, which belong to C=O and C=C stretching vibrations in HMF, respectively, illustrating the co-existence of 2-formylfuran ring linked into humin structure assumably via intermolecular dehydration of O-H groups instead of aldehyde group in HMF [5]. Other characteristic bands observed in fructose humins are bands at ca. 3300 cm^{-1} attributed to O-H stretching vibration, 3120 cm^{-1} assigned to aromatic C-H stretching vibrations, 2925 cm^{-1} assigned to aliphatic C-H stretching vibration, and 1705 cm^{-1} assigned to C=O stretching vibrations conjugated with C=C [10]. At the early stage, HMF intermediate from fructose dehydration exists abundantly in the reaction system, therefore HMF can take part in humin formation through two reactive sites, including aldehyde group predominantly and hydroxyl group.

With the rise of reaction time from 12 to 50 min, HMF intermediate was completely converted (Fig. 1). Humins can react further on aldehyde groups, as evidenced by the disappearance of the band at 1674 cm^{-1} assigned to C=O stretching vibrations in 2-formylfuran rings. Consequently, the band of C=C shifted from 1591 to 1616 cm^{-1} , and the band of O-H stretching vibrations moved to higher wavenumber of 3388 cm^{-1} , presumably resulting from aldol addition and condensation of aldehyde C=O groups. The three bands at 1510, 1026 and 804 cm^{-1} ascribed to furan rings vibrations continued to increase and dominated as polyfuranic units incorporated into humin structure. At this stage, when HMF intermediate was completely converted, humins can react further on aldehyde groups, as evidenced by disappearance of 2-formylfuran rings.

When the reaction was prolonged till 12 h, three bands of furan rings at 1510, 1026 and 804 cm^{-1} as well as the band of aromatic C-H stretching vibrations at 3120 cm^{-1} decreased and became obscure, whereas the band of C=C at 1616 cm^{-1} visibly increased, suggesting the opening of furan rings and dehydrogenation of aromatic hydrogen accompanied by further aromatization. The increased aromaticity was confirmed by the decrease of H/C ratio

from 0.724 to 0.686 through elemental analyses of humins after reaction for 80 min and 12 h, also in line with the literature report that humin polyfuranics reacted further through intramolecular condensation, dehydration and decarboxylation reactions to generate extensively aromatic networks [11]. At the later stage, if the reaction time was long enough, humins can undergo subsequent aromatization, with the furan rings reduced and the C=C groups increased.

According to SEM images (Fig. 3), humins derived from fructose at early stages are mainly consisted of isolated and interconnected spherical particles. The average diameter of spherical particles grows from ca. 1 μm (Fig. 3a-b) to 3 μm (Fig. 3c-d) with the increase of reaction time from 12 to 50 min. After reaction for 12 h, similar to H_2SO_4 -catalyzed fructose conversion [6], agglomerated particles were observed resulting from further aromatization (Fig. 3e-f), which is in consistency with the IR analysis.

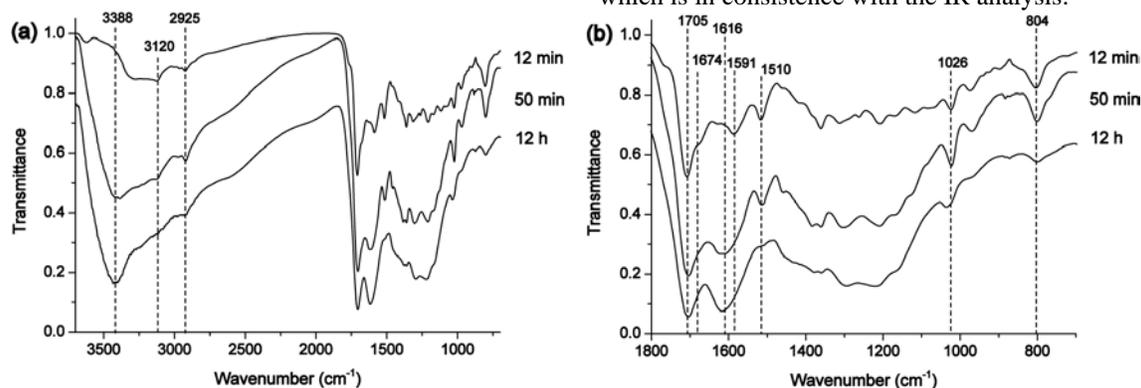


Figure 2. IR spectra of fructose humins: (a) 3700-700 cm^{-1} ; (b) 1800-700 cm^{-1} . Conditions: 0.925mmol fructose, 1.000 g $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$, 6.000 g H_2O , 170 $^\circ\text{C}$.

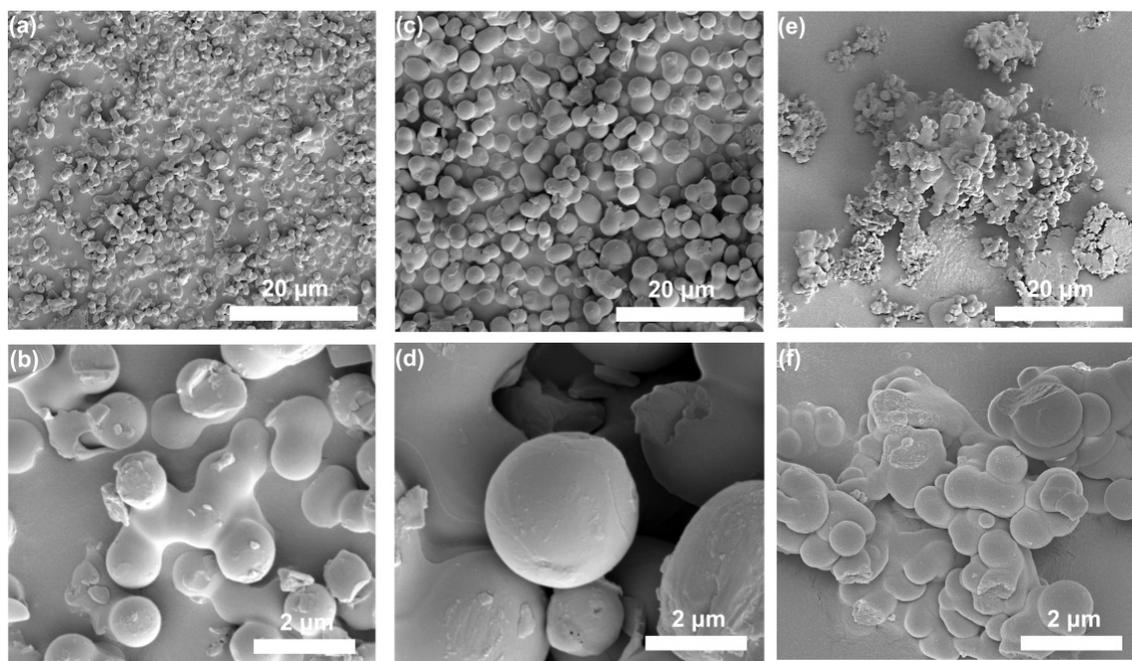


Figure 3. SEM images of humins formed during fructose conversion after reaction for (a-b) 12min, (c-d) 50 min, (e-f) 12 h. Conditions: 0.925mmol fructose, 1.000 g $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$, 6.000 g H_2O , 170 $^\circ\text{C}$.

IV. CONCLUSIONS

In summary, fructose was efficiently converted into LA with a high yield of 76% by catalysis of acidic ionic liquid in water. Through investigation on chemical structures and morphologies of humin byproduct, it was inferred that formation of fructose humins went through three stages for

the first time. At the early stage, HMF intermediate from fructose dehydration can participate in humin structure through both aldehyde group predominantly and hydroxyl group. When HMF intermediate was completely converted, humins can undergo further reactions on aldehyde groups, with disappearance of 2-formylfuran rings. If the reaction time was long enough, humins can aromatize subsequently

by reducing the furan rings and increasing the amount of C=C.

ACKNOWLEDGMENT

This project was supported by the Fundamental Research Funds for the Central Universities (DUT15LK17).

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