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Short communication

NaOH catalyzed condensation reactions between levulinic acid and biomass derived furan-aldehydes in water

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ABSTRACT

NaOH catalyzed condensation reaction between 5-hydroxymethylfurfural and levulinic acid in water gives a 2.5: 1 mixture of aldol products: (*E*)-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid and (*E*)-3-[5-(hydroxymethyl)furan-2-yl]methylene-4-oxo-pentanoic acid in 82% combined yield. A similar reaction between furfural and levulinic acid gives the linear polymer, poly[1-carboxymethyl-4-(furan-2-yl)-2-oxo-butane-1,4-diyl] in 91% yield.

1. Introduction

The increasing concern over declining petroleum reserves has promoted the current explorations for renewable resources based fuels as well as platform chemicals for chemical and polymer industries. Triglycerides, succinic acid, lactic acid, glycerol, 5-hydroxymethylfurfural (HMF, **1**), furfural (F, **2**), and 4-oxopentanoic acid or levulinic acid (LA, **3**) produced from plant based biomass are in the forefront of this new generation of feedstocks (Gallezot, 2012; Climent et al., 2014; Gandini, 2008). 5-Hydroxymethylfurfural and furfural have found a special place in this category of chemicals as these furan-aldehydes are dehydration products of C-6 and C-5 sugars derived from depolymerization of the key biomass polysaccharides cellulose and hemicellulose (Amarasekara, 2011; Hu et al., 2012; Gandini, 2010). During the acid catalyzed dehydration of C-6 sugars to produce HMF, depending on the reaction conditions this furan can undergo rehydration as a subsequent step, resulting a fragmentation to levulinic and formic acids. The C-5 keto acid formed is a versatile building block for the synthesis of various chemicals such as levulinate esters, γ-valerolactone, 1,4-pentanediol, α-angelica lactone, 2-methyltetrahydrofuran (Lange et al., 2012), and δ-amino levulinic acid (Sheldon, 2014). A number of these LA derivatives have been used as building blocks for the preparation of polymers as well as fuel precursors (Climent et al., 2014; Alonso et al., 2013; Amarasekara and Hawkins, 2011; Amarasekara and Wiredu, 2014a). Aldol condensation of furfural and 5-hydroxymethylfurfural with acetone is known to yield typical aldol products in 1:1 molar ratio reaction and excess aldehyde yields double-aldol condensation products (West et al., 2008; O'Neill et al., 2013).

Dumesic and co-workers first investigated the aldol condensation of furan aldehydes and a series of ketones in THF-aq. NaOH as a synthetic approach to build C-6-15 range molecules that could be converted to deoxygenated liquid transportation fuels (West et al., 2008; Chheda and Dumesic, 2007; Barrett et al., 2006). In addition, Patel et al. reported the self-polycondensation of the acetone-furfural adduct, 2-furfurylidene methyl ketone to give a furfural-acetone polymer when refluxed in aq. NaOH (Patel and Patel, 1983). Recently, we have shown that cellulose or dry corn stover powder can be directly converted to a mixture of HMF and furfural–acetone aldol condensation products in a single-reactor operation by heating in acetone at 120 °C in the presence of Brønsted acidic ionic liquid catalysts (Amarasekara and Wiredu, 2014b). Where ionic liquid was used as a multi-purpose catalyst for depolymerization, dehydration and aldol condensation reactions. Aldol condensation between furfural and levulinic acid is known to give δ-furfurylidenelevulinic acid in low yields when Na_2CO_3 is used as the base in water and water–ethanol mixtures (Hachihama and Hayashi, 1954; Iwakura and Hayashi, 1960). In addition Subbiah et al. have recently reported the formation of 2,5-dihydroxymethylfurfural and 5-hydroxymethyl furanoic acid from HMF in aq. NaOH *via* Cannizzaro reaction (Subbiah et al., 2013).

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However, as far as we are aware there are no reports on aldol condensations between 5-hydroxymethylfurfural and levulinic acid. Our interests (Amarasekara and Hawkins, 2011; Amarasekara et al., 2009, 2012;) in preparation of renewable resources based building blocks as polymer and fuel precursors has led us to explore the NaOH catalyzed condensation reactions between levulinic acid and biomass derived furan-aldehydes.

2. Materials and methods

2.1. General methods

Levulinic acid, 5-hydroxymethylfurfural, furfural and sodium hydroxide (99.9%) were purchased from Aldrich Chemical Co. ^{1}H NMR Spectra were recorded in DMSO-d_6 or $CDCl_3$ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS (δ = 0.00). ^{13}C Chemical shifts were measured relative to DMSO-d_6 and converted to δ (TMS) using δ (DMSO) = 39.51, and in $CDCl_3$ converted to δ (TMS) using δ ($CDCl_3$) = 77.00. FT-IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets. UV–vis Spectra were recorded on a Carey 50 UV–vis spectrophotometer using 1 cm quartz cells. Number average molecular weight M_n and polydispersity index (PDI) of the polymer samples were measured on a Waters gel permeation chromatography (GPC) system with Waters Styragel columns, UV detector and using tetrahydrofuran (THF) as the solvent. Elemental analysis was performed at QTI laboratories, New Jersey, USA. Thermogravimetric analysis was carried out in air on a Perkin Elmer Diamond TG/DTA system in 25–800 °C temperature range, 10 °C/min, and using Pt crucibles.

2.2. NaOH catalyzed condensation reactions between levulinic acid and 5-hydroxymethylfurfural

A mixture of 5-hydroxymethylfurfural (0.880 g, 6.984 mmol) and levulinic acid (2.025 g, 17.46 mmol) in 3 mL of water was cooled in an ice bath. Sodium hydroxide (0.754 g, 18.86 mmol) was dissolved in 6 mL of water, cooled to 0 °C and added into the stirred levulinic acid, HMF mixture and allowed to warm to room temperature in about an hour. The mixture was further stirred at room temperature for 48 h, and then acidified with 1.0 M aq. HCl. The resulting solution was extracted with methylene chloride (3 × 15 mL) and the combined methylene chloride layer was washed with water (3 × 10 mL), dried (anhydrous Na_2SO_4) and concentrated in the rotary evaporator to give the crude product as a yellow oil. Which was chromatographed on silica, eluting with 2–15% methanol in methylene chloride to give two products.

Major product: **4**, (*E*)-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid. Colorless viscous oil, 0.916 g, 58.6% yield.

Anal. Calc. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39. Found: C, 58.66; H, 5.60. UV (MeOH) λ_{max} 320 nm. IR (KBr) 706, 770, 953, 1022, 1191, 1280, 1404, 1521, 1671, 2847, 2917, 3388 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, TMS) δ 2.71 (2*H*, t, *J* = 6.8 Hz, CH_2), 2.93 (2*H*, t, *J* = 6.8 Hz, CH_2), 3.82 (1*H*, bs, OH), 4.65 (2*H*, s, $C\underline{H}_2$—OH), 6.39 (1*H*, d, *J* = 3.2 Hz, Fu), 6.62 (1*H*, d, *J* = 3.2 Hz, Fu), 6.65 (1*H*, d, *J* = 15.6 Hz, =CH—CO), 7.31 (1*H*, d, *J* = 15.6 Hz, =C<u>H</u>—Fu), 11.10 (1*H*, bs, COOH). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C, TMS) δ 29.7, 35.6, 57.6, 110.6, 117.1, 122.6, 129.1, 150.8, 156.8, 177.1, 197.6.

Minor product: **5A**, (*E*)-3-[5-(hydroxymethyl)furan-2-yl]methylene-4-oxo-pentanoic acid. Colorless viscous oil, 0.367 g, 23.4% yield.

Anal. Calc. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39. Found: C, 58.61; H, 5.54. UV (MeOH) λ_{max} 320 nm. IR (KBr) 709, 792, 884, 1068, 1049, 1180, 1277, 1378, 1626, 1650, 2920, 2973, 3419 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, TMS) δ 2.42 (3*H*, s, CH_3), 3.74 (2*H*, s, CH_2), 4.20 (1*H*, bs, OH), 4.55 (2*H*, s, $C\underline{H}_2$—OH), 6.36 (1*H*, d, *J* = 3.2 Hz, Fu), 6.67 (1*H*, d, *J* = 3.2 Hz, Fu), 7.28 (1*H*, s, =C<u>H</u>—Fu), 11.25 (1*H*, bs, COOH). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C, TMS) δ 25.2, 29.7, 57.1, 110.2, 118.6, 128.7, 130.1, 150.3, 157.9, 176.6, 199.2.

2.3. NaOH catalyzed condensation reaction between levulinic acid and furfural

A mixture of furfural (0.960 g, 10.00 mmol) and levulinic acid (1.160 g, 10.00 mmol) in 20 mL water was cooled in an ice bath. Sodium hydroxide (0.680 g, 17.00 mmol) was dissolved in 30 mL water, cooled to 0 °C and added into magnetically stirred levulinic acid furfural mixture and allowed to warm to room temperature in about an hour. The mixture turned to yellow in 1–2 min, to dark brown in about 5 min, and was further stirred at room temperature for 48 h. Then acidified with 1.0 M aq. HCl; while acidification polymeric product separated as a pale yellow solid mass, which was filtered and repeatedly washed with deionized water (200 mL) to remove acid and salts. The crude polymer was dried in air and purified by soxhlet extraction for 20 h, using cyclohexane as the solvent.

Poly[1-carboxymethyl-4-(furan-2-yl)-2-oxo-butane-1,4-diyl] (**8**), 1.765 g, 91% yield. Anal. Calc. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.55; H, 5.28.

^{1}H and ^{13}C NMR spectra of the polymer **8** are in the article (Fig. 3a and b); IR spectrum and TGA-DTGA plot are in the Supplementary material Figs. 4 and 5.

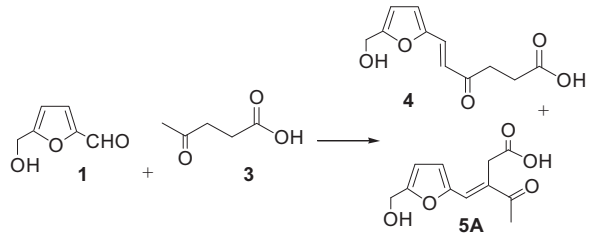

Fig. 1. Aldol condensation of 5-hydroxymethylfurfural (HMF, **1**) with levulinic acid (LA, **3**) in aq. NaOH, **4**:**5A** = 2.5:1.

Table 1
The relative energies of linear HMF-LA adduct **4** and selected isomeric structures of branched HMF-LA adducts (**5A**-**C**) calculated using 6-311++*G*(*d*′) basis set (kcal/mol).

Isomeric structure	ΔE° (solv)	ΔE°	ΔE°_{ZPE}	ΔH°	ΔG°
4	0.00	0.00	0.00	0.00	0.00
5A	1.90	−0.98	−1.21	−1.27	0.55
5B	6.80	3.39	3.24	3.13	4.69
5C	9.73	7.92	7.43	7.51	8.45

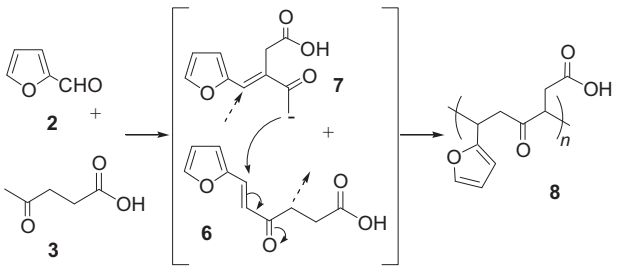

Fig. 2. Aldol-Michael polymerization of furfural (F, **2**) with levulinic acid (LA, **3**) in aq. NaOH producing poly[1-carboxymethyl-4-(furan-2-yl)-2-oxo-butane-1,4-diyl] **8**.