Synthesis of biomass-derived feedstocks for the polymers and fuels industries from 5-(hydroxymethyl)furfural (HMF) and acetone

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ARTICLE

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We show that 5-(hydroxymethyl) furfural (HMF) and acetone can be selectively converted to a range of biomass-derived high molecular weight chemicals in high yield (> 90%). HMF was condensed with acetone and purified to produce an HMF-Acetone-HMF dimer (HAH). We then selectively synthesized various compounds from HAH by the sequential catalytic reaction pathway of hydrogenation, ring-opening, and hydrodeoxygenation. These synthesized HMF-derived chemicals were characterized by 1D and 2D NMR spectra and high resolution mass spectrometry (HRMS). The HMF-derived molecules described in this paper can be feedstocks for the polymer, pigment, and petroleum industries.

Introduction

Growing environmental concerns surrounding the increasing carbon dioxide emissions, with the increased use of non-renewable fossil resources, have resulted in increased research efforts in the development of routes for sustainable production of fuels and chemicals. Carbohydrates, the most abundant fraction of biomass, are readily available as feedstocks for the production of biomass-derived renewable and sustainable chemicals. Unlike fossil-based feedstocks, carbohydrates are rich in oxygenated functional group which is advantageous for the production of building block chemicals, as hazardous and expensive oxidative methods are not required for upgrading carbohydrates to functional platform and/or commodity chemicals. However, efficient methods are required for the selective removal and/or modification of excess functional groups to produce desired platform and/or commodity products.[1] Additionally, a successful bio-refinery must produce high-value chemical precursors or products to be cost-competitive with conventional oil-refinery. A niche, however, challenging area for generating high revenue from renewable resources like biomass derived platform molecule is to produce monomers for functional polymers and chemicals for dyes and pigment industry.

One biomass-derived versatile platform molecule is 5-(hydroxymethyl)furfural (HMF). HMF is produced by selective dehydration of biomass-derived carbohydrates and has gained considerable attention in recent years. Various methods utilizing single as well as bi-phasic systems have been developed for the production of HMF from carbohydrates.[2–4] Additionally, HMF can also be produced from food waste.[5–7] Efficient production of HMF from biomass-derived carbohydrates was recently demonstrated using acetone-water solvent system.[8] HMF is an important precursor for the production of renewable chemicals[9], polymers[10,11], and biofuels.[12] HMF can be converted to 2,5-furandicarboxylic acid (FDCA) which has the potential to replace terephthalic acid in the production of polyethylene terephthalate (PET). Production of FDCA from HMF has been demonstrated with high yield.[13,14] Avantium and BASF had plans to produce FDCA on an industrial scale (50 kton/year) by 2024, although this effort has now been canceled.[15] While the majority of industrial interest on HMF utilization is primarily focused on the production of FDCA, there is a range of other chemicals that can be produced from HMF.[16] 1,6-hexanediol, a monomer used in the production of polyester polyols and polycarbonate diols, can be produced from HMF-derived tetrahydrofuran-dimethanol (THFDM).[17,18] Hydrodeoxygenation of HMF can produce 2,5-dimethyl furan (DMF), a gasoline additive.[4,19]

Another approach to utilize HMF as a platform molecule is to synthesize higher molecular weight chemicals that are precursors to functional polymers and organic pigments. Compared to low molecular weight chemicals like FDCA and 1,6-hexanediol, high molecular α-ω diols are reported to improve the control over various polymer properties, such as mechanical strength, glass transition temperature, and the thermal resistance of polymer.[20] Additionally, to make diesel and jet fuel range alkanes containing between 8-15 carbon atoms from biomass-derived platform molecule like HMF, C-C bond formation reactions are required. High molecular weight compounds obtained from HMF can undergo hydrodeoxygenation reactions to produce alkanes with similar properties as diesel and jet fuel range molecules. Aldol condensation of HMF with a ketone results in higher molecular weight molecules which can be used to produce long chain hydrocarbons suitable for replacing diesel after further

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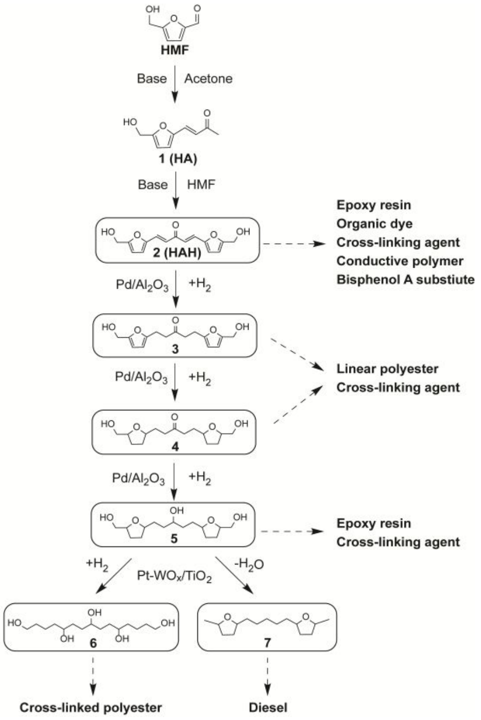
hydrodeoxygenation.[21] The product from HMF and acetone (or another ketone) condensation is an α-ω functionalized diol that may be suitable for polymeric application after different reduction treatments.[21]

Both acid[22] and base catalysts[23] have been reported to catalyze self-condensation of HMF as well as aldol condensation of HMF with a ketone. However, base-catalyzed condensation is favored over acid catalyst condensation as acid-catalyzed aldol condensation produces undesired humins due to self-condensation of HMF under acidic condition.[24] Aldol condensation of HMF and acetone over various basic homogeneous and heterogeneous catalysts has been reported.[12,25–27] However, the product distribution after aldol condensation of HMF and acetone was broad and all the products were not characterized.[28] Furthermore, hydrogenation and hydrodeoxygenation of aldol condensation products over heterogeneous catalysts has been reported to be non-selective due to C-C bond cleavage under the harsh reaction conditions employed.[21,29,30] Thus, there still remain significant challenges, including the poor selectivity to desired high molecular weight chemicals during condensation reaction, harsh reaction conditions required for hydrogenation and hydrodeoxygenation reactions, and the use of expensive purification steps to obtain polymer grade chemicals. These limitations have confined the applications of these high molecular weight chemicals to the production of drop-in liquid fuels.[21,28] Therefore, selective production, characterization and simple purification of high molecular weight chemicals are required for broadening the application of biomass-derived high molecular weight chemicals to functional polymers and organic dyes.

In this paper, we demonstrate the selective production of higher molecular weight chemicals (see Scheme 1) derived from the aldol condensation of HMF and acetone. We describe how these molecules can be selectively produced in high yields (> 90%). We identify the appropriate reaction conditions for the selective condensation of HMF and acetone to either **1** (HA) or **2** (HAH). We show that an α-ω diol (**2**) is produced by condensation of two HMF molecules with one acetone molecule. It should be noted that **2** is a candidate for the production of conductive polymers due to the connected *p*-orbitals with delocalized electrons[31], or as an epoxy resin replacement for bisphenol-A (BPA) (after etherification with epichlorohydrin (ECH)).[10] Additionally, **2** could be used as a yellow organic dye since the conjugated bonds absorb light in the blue region of the visible spectrum (see Figure S1). Partial and complete hydrogenation of **2** produces **3** and **4**, respectively. Both **3** and **4** can be used as polyester precursors after esterification with methacrylic acid (MAA).[32] We note here that saturation of double bonds, by selective hydrogenation, of **2**, **3**, and **4** can affect the reactivity of these monomers during polymerization, and as such these compounds can be used as cross-linking agents in various coating to tune the curing time required for diverse applications. Additionally, **5** itself can be used as a cross-linking agent with citric acid for the formation of epoxy resin.[33] Furthermore, we show that **5** can be converted to **6** and **7** by ring-opening and hydrodeoxygenation over Pt-WO_x/TiO_2 catalysts. **6** is a symmetric aliphatic polyol with two terminal and three secondary hydroxyl groups. **6** is expected to be used as a monomer in the production of cross-linked polyester[34], and **7** could be converted to diesel after de-etherification[12] or used directly as a diesel additive.



Scheme 1. Reaction pathways for synthesis of high molecular weight biomass-derived molecules from HMF and acetone with their potential applications.

Experimental

Materials

HMF (97%, Alfa Aesar & 98% AK Scientific), acetone (HPLC grade, Fisher Scientific), methanol (HPLC grade, Fisher Chemical), NaOH (FCC specification, Fisher Scientific), HCl (37 wt%, Sigma-Aldrich), ethyl acetate (HPLC grade, Fisher Chemical), hexane (HPLC grade, Sigma-Aldrich), quartz wool (Ohio Valley Specialty), silica gel (Davisil grade, Sigma-Aldrich), 2-propanol (HPLC grade, Sigma-Aldrich), 5 wt% Pd/alumina (Strem Chemicals), ammonium tungsten oxide hydrate (Alfa Aesar), TiO_2 support (99.7%, <25 nm particle size, Sigma-Aldrich), Chloroplatinic acid solution (8 wt% in H_2O, ACS reagent, Sigma-Aldrich) were used as received. Milli-Q water (~18 MΩ-cm) was used in all experiments. Condensation reactions were performed in a thick-walled glass reactor (Chromatography Research Supplies). Hydrogenation and hydrodeoxygenation reactions were performed in a 50 mL Parr reactor (Parr Instrument Company).

Pt-WO_x/TiO_2 catalyst preparation

Synthesis of WO_x/TiO_2 supports

WO_x/TiO_2 support was prepared by wet impregnation of ammonium tungsten oxide hydrate on TiO_2, as reported by He et al.[11] Briefly, 0.93 g of ammonium tungsten oxide hydrate was dissolved in 100 mL Milli-Q water. 37 wt% HCl was added dropwise to ammonium tungsten oxide hydrate solution to pH 1. This solution was refluxed at 353 K for 12 h. 6 g of TiO_2 was added to the solution and the solid suspension was refluxed at 353 K for 30 min. Water was removed at 333 K under vacuum (50 mbar). The WO_x/TiO_2 powder obtained after vacuum evaporation was further dried at 383 K for 12 h. The dried WO_x/TiO_2 powder was calcined under air flow (100 mL/min) at 673 K for 3 h (with a ramp rate of 1 K/min).

Impregnation method to prepare Pt-WO_x/TiO_2

Pt-WO_x/TiO_2 catalysts was synthesized by conventional wet impregnation using chloroplatinic acid as a Pt precursor. Briefly, 30 mL 4 wt% chloroplatinic acid solution was added to 6 g WO_x/TiO_2 support and the solid suspension was stirred at 353 K to evaporate water. The solid after water evaporation was further dried at 353 K in a vacuum oven for 12 h. Finally, the dried solid was grounded to a powder and was calcined under air flow (100 mL/min) at 673 K for 3 h (with a ramp rate of 1 K/min) and subsequently reduced under H_2 flow (100 mL/min) at 523 K for 2 h. The reduced catalysts were cooled to room temperature by natural convection. The reduced catalyst was passivated with 1% O_2 in Ar.

Characterization and quantification of products

HPCL analysis of HMF, 1 (HA), and 2 (HAH)

HMF and products of aldol condensation (**1**, **2**) were quantified by High Performance Liquid Chromatography (HPLC) analysis. The as-synthesized product solution after aldol condensation was neutralized with HCl (pH of the solution was measured by pH test strips) and diluted 9 times in methanol to dissolve the precipitated HAH (**2**). The diluted sample was analyzed to determine the concentration of HMF and **1**. The 9 times diluted product mixture was further diluted 63 times in methanol for the analysis of **2** to avoid saturation of the PDA detector. The diluted samples were filtered with 0.2 µm PTFE membrane filter before analysis. The concentrations of **1**, **2**, and HMF were measured by a Waters 2695 separations module equipped with a Luna C18 (Phenomenex, Part No. 00G-4041-E0) HPLC column and a Waters 2998 PDA detector, set at 320 nm (for HMF analysis) and 390 nm (for **1**, **2** analysis). The temperature of the HPLC column was held constant at 323 K. The mobile phase was a gradient methanol/water (with 0.1 wt% formic acid) at a constant flow rate of 1.0 mL/min (0.1 wt% formic acid water linearly changed to methanol in 20 min, pure methanol for 7 min, and methanol was linearly changed to 0.1% formic acid water in 3 min). Purified standards of **1** (see below) and **2** (see below) were used for calibration. Carbon balance, product selectivity, and conversion were calculated by Equations 1–5.

$$\text{Total carbon balance} =$$

$$\frac{\text{Moles of final HMF} + \text{Moles of final HA} + 2\cdot\text{Moles of final HAH}}{\text{Moles of initial HMF}}\cdot 100\ (\%) \qquad (1)$$

$$\text{Total product yield} =$$

$$\frac{\text{Moles of final HA} + 2\cdot\text{Moles of final HAH}}{\text{Moles of initial HMF}}\cdot 100\ (\%) \qquad (2)$$

$$\text{HA selectivity} = \frac{\text{Moles of final HA}}{\text{Moles of final HA} + \text{Moles of final HAH}}\cdot 100\ (\%) \qquad (3)$$

$$\text{HAH selectivity} = \frac{\text{Moles of final HAH}}{\text{Moles of final HA} + \text{Moles of final HAH}}\cdot 100\ (\%) \qquad (4)$$

$$\text{HMF conversion} =$$

$$\frac{\text{Moles of initial HMF} - \text{Moles of final HMF}}{\text{Moles of initial HMF}}\cdot 100\ (\%) \qquad (5)$$

GC-FID analysis of 4, 5, 6, and 7

4, **5**, **6**, and **7** were quantified by gas chromatograph (Shinadzu GC-2010) equipped with a flame-ionization detector and a Zebron ZB-50 column (Phenomenex, Part No. 7HG-G004-11). The product solution (without dilution) was filtered with 0.2 µm PTFE membrane filter before GC analysis. Analytical standards of **4** and **5** were synthesized (see below) and GC was calibrated with these analytical standards. Since, analytical standards of 6 and 7 couldn't be made they were quantified using effective carbon number (ECN) analysis.[35] **6** (ECN = 11.75) and **7** (ECN = 13) (see Figure S10) using pentadecane (ECN = 15) as internal standard.

UHPLC-QTOF analysis of 6

5 was reacted over Pt-WO_x/TiO_2 catalysts at 383 K to prepare the sample for analysis. The sample was filtered through a 0.2 μm PTFE membrane filter before UHPLC analysis. Analysis was performed on a Shimadzu Nexera-X2 UHPLC equipped with a Kinetex 1.7 μm XB-C18 (Phenomenex) UHPLC column, a SPD-M30A PDA detector and a Bruker impact II QTOF mass spectrometer (negative mode). The temperature of the column was held constant at 383 K. The mobile phase was a gradient methanol/water (with 0.1 wt% formic acid) at 0.6 mL/min flow rate (10% methanol linearly changed to pure methanol in 3 min, pure methanol for 0.2 min, and pure methanol was linearly changed to 10% methanol in 0.1 min). Data were processed by Bruker Compass Data Analysis software (v5.1).

Synthesis and purification of products

Selectivity control of 1 and 2 by aldol condensation

Molar ratio of 1 to 2 = 12

89 mg of HMF was dissolved in a solution containing 0.5 ml acetone and 0.48 ml Milli-Q water in a 10 mL glass vial. A cross-shaped stir bar was added to the glass vial for mixing and the solution was heated to 308 K in an oil bath. The solution was kept at 308 K for 15 min before addition of 0.135 ml 1 M NaOH solution. The solution was stirred (800 rpm) at 308 K for 10 min. After the required time had elapsed, 1.11 ml 0.1 M HCl solution was added to terminate aldol condensation reaction.

Molar ratio of 1 to 2 = 0.9

142 mg HMF was dissolved in a solution containing 0.1 ml acetone and 0.98 ml Milli-Q water in a 10 mL glass vial. A cross-shaped stir bar was added to the glass vial for mixing and the solution was heated to 308 K in an oil bath. The solution was kept at 308 K for 15 min before addition of 0.037 ml 3 M NaOH solution. The solution was stirred (800 rpm) at 308 K for 20 min. After the required time had elapsed, 0.14 ml 0.5 M HCl solution was added to terminate aldol condensation reaction.

Molar ratio of 1 to 2 = 0.04

273 mg of HMF was dissolved in a solution containing 0.08 ml of acetone and 1.90 ml of Milli-Q water in a 10 mL glass vial. A cross-shaped stir bar was added to the glass vial for mixing and the solution was heated to 308 K in an oil bath. The solution was kept at 308 K for 15 min before addition of 0.18 ml 3 M NaOH solution. The solution was stirred (800 rpm) at 308 K for 60 min. After the required time had elapsed, 0.75 ml 0.5 M HCl solution was added to terminate the aldol condensation reaction.

Purification of 1 (HA) by column chromatography

Column chromatography was used to isolate HA and produce an analytical standard for quantification. Prior to separation, acetone and water were evaporated at 313 K, under vacuum (50 mbar) from the product mixture obtained after aldol condensation (see above). The concentrated product solution was separated on a silica gel column. Ethyl acetate/hexane (50/50 (v/v)) was used as the eluent. Purified HA solution (light yellow liquid) was collected. Ethyl acetate and hexane were evaporated at 313 K, under vacuum (50 mbar). The purity of HA was determined by ^1H and ^{13}C NMR (see Figure S5). The purified HA was used as the calibration standard for HPLC analysis (see Figure S7).

Purification of 2 (HAH) by filtration

HAH was purified by precipitation in water. The solution obtained after aldol condensation using acetone/HMF molar ratio of 0.5 was neutralized. The neutralized solution was diluted 6.5 times with water leading to HAH precipitation. Precipitated HAH was separated by vacuum filtration. After separation, purified HAH was dried overnight in an oven at 333 K to remove residual water. The purity of the dried HAH was analyzed by ^1H and ^{13}C NMR (see Figure 4). The purified HAH was used as the calibration standard for HPLC analysis (see Figure S8).

Production of 3 by hydrogenation

HAH hydrogenation was conducted in a flow-through reactor consisted of a 6 inch stainless steel tube with corresponding stainless steel valves and fittings (Swagelok). The reactor was placed between two aluminum blocks inside an insulated furnace. A type-K thermocouple (Omega) was placed at the reactor wall to monitor and control the reaction temperature using a 16 A series controller (Love). 50 mg 5 wt% Pd/Al_2O_3 diluted 10 times with α-alumina was used as the catalyst. The catalyst was packed in the reactor and between two quartz wool plugs. The as-synthesized HAH product solution was diluted 50 times with methanol to prepare the feed solution for hydrogenation. The feed solution (0.1 mL/min) and H_2 gas (24 mL/min) were passed through the reactor at a WHSV of 93.2 h^{-1} at 393 K, under 62 bar H_2 back pressure to produce **3**. The solvent was evaporated and the product was characterized by ^1H and ^{13}C NMR (see Figure S2).

Production of 4 by hydrogenation

The flow-through reactor system, described above, was used to produce **4**. 100 mg of 5 wt% Pd/Al_2O_3 diluted 20 times with α-alumina was used as the catalyst. The catalyst was packed in the reactor and between two quartz wool plugs. The as-synthesized HAH product solution was diluted 60 times with methanol to prepare the feed solution. The feed solution (0.1 mL/min) and H_2 gas (24 mL/min) were passed through the reactor at a WHSV of 46.7 h^{-1} at 423 K, under 62 bar H_2 back pressure to produce **4**. The solvent was evaporated and the product was characterized by ^1H and ^{13}C NMR (see Figure S3)

Production of 5 by hydrogenation

460 mg purified HAH was dissolved in 30 mL 2-propanol/water (80/20 (v/v)) solvent. 60 mg 5 wt% Pd/Al_2O_3 and the HAH solution were added to a 50 mL Parr reactor. The reactor was purged twice with 14 bar Ar and three times with 30 bar H_2. The reactor was pressurized to 30 bar H_2 and was heated to 453 K in 1 h (final pressure increased to 55 bar at 453 K). The reactor was kept at 453 K for 8 h and then cooled to room temperature by natural convection. Hydrogenated product was separated from the solid catalyst by filtration. Solvent was evaporated and the

product was characterized by ^{1}H and ^{13}C NMR (Figure S3 and S4) and was quantified by GC-FID.

Production of 6 and 7 by hydrodeoxygenation and ring-opening

72 mg passivated Pt-WO_x/TiO_2 catalysts was reduced at 523 K, under 20 bar H_2 in the Parr reactor. 8.4 g of as-synthesized **5** solution was injected into the reactor using HPLC pump. The reactor was pressurized with 30 bar H_2 and heated to 433 K in 1 h. The reactor was kept at 433 K for 24 h and then cooled to room temperature by natural convection. The pressure in the reactor was 50 bar at 433 K. **6** and **7** were characterized by 1D and 2D NMR (Figure S6), UHPLC-QTOF, and high resolution mass spectrometry (HRMS). **6** and **7** were quantified by GC-FID with ECN analysis.[35]

Results and Discussion

Selectivity control of aldol condensed products

Aldol condensation of HMF and acetone produces multiple products, including the desired products, HA and HAH, as well as undesired degradation products. As shown in Figure 1, by operating at 308 K and low NaOH concentration (~110 mM) the production of undesired self-condensation products is eliminated. The selectivity to a particular product, HA or HAH, can be controlled by changing the ratio of initial concentration of acetone and HMF as shown in Figure 1(a). 93% selectivity of HA was achieved when the initial molar ratio of acetone to HMF was 9.5. High initial concentration of acetone accelerates the formation of HA compared to HAH, leading to the selective production of HA. When condensing a stoichiometric feed (acetone to HMF molar ratio of 0.5), HA is initially formed and subsequently converted to HAH (see Figure 4(b)). However, when the initial molar ratio of acetone to HMF is 1.2, both HA and HAH are produced in nearly equal concentrations (see Figure 1(a)) with 48% and 52% selectivity to HA and HAH, respectively. Self-condensation and other degradation reaction can be eliminated with an overall carbon balance of > 92% (see Figure 1(b)) with different initial molar ratio of acetone to HMF under the low NaOH concentration (~110 mM) and low reaction temperature (308 K). It should be noted that the carbon balance was greater than 96% when one product was targeted (see Figure 1(b)).

Degradation of aldol condensation products

Base-catalyzed degradation of HMF and the products of aldol condensation can be problematic during the production of high molecular weight chemicals from HMF. It can be seen from Figure 2 that the total carbon balance was greater than 95% at 55 min, at which point HMF conversion was 93%. However, at complete conversion of HMF, the total carbon balance decreased to 81%, due to the increased condensation of HA and HAH in presence of base. Therefore, neutralization of NaOH at near complete conversion of HMF is important to prevent product degradation and achieve high yield of the desired product.

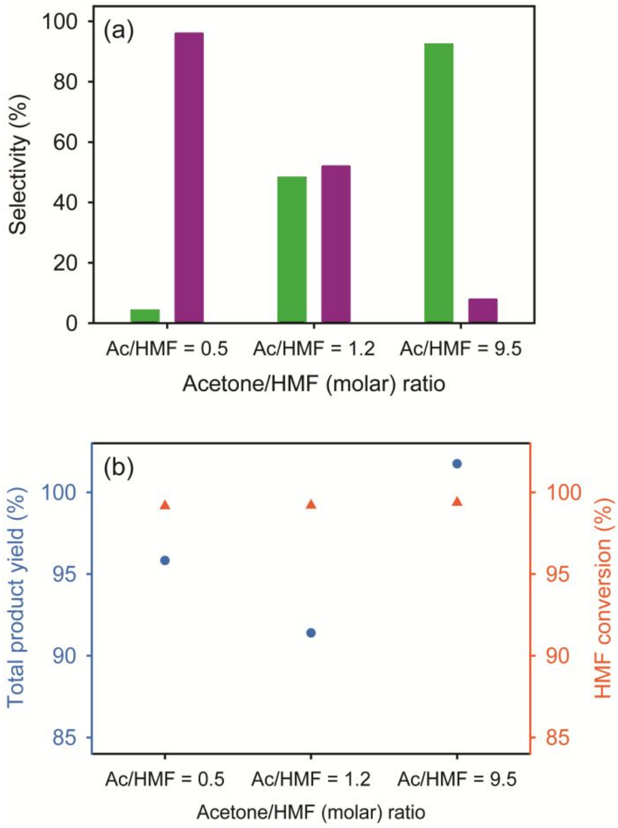


Figure 1. (a) Product selectivity (Green: HA, Purple: HAH), (b) Total product yield and HMF conversion for aldol condensation of HMF with acetone as a function of the acetone (Ac) to HMF molar feed ratio at 308 K (Blue: Total product yield, Orange: HMF conversion). Selectivity was measured at 99% HMF conversion.

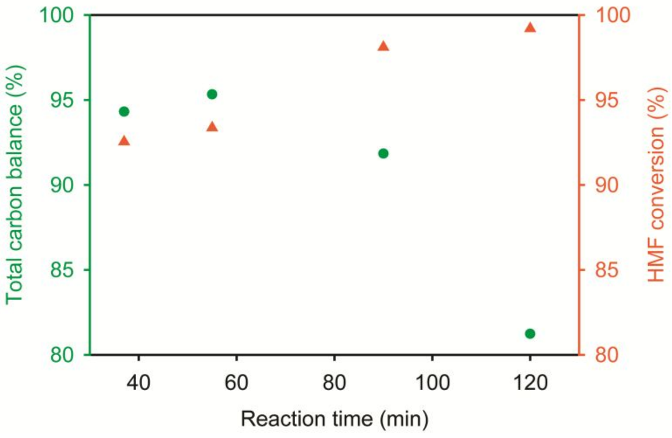


Figure 2. Total carbon balance for aldol condensation of HMF and acetone as a function of reaction time. Reaction conditions: [Ac] = 0.53 M, [HMF] = 1.06 M, [NaOH] = 0.11 M at 308 K (Green: Total carbon balance, Orange: HMF conversion).

Purification of aldol condensation products

Column chromatography was used to successfully separate HA from HAH, by-products, and residual HMF (see Figure S5). We focused our attention on the separation of HAH as, unlike HA, HAH is chemically stable and is a symmetrical α-ω diol with potential industrial applications (see Scheme 1). HAH has low solubility in water and precipitates out of the product solution with dilution.

Specifically, HAH solubility in water was determined to be 1.08 mg/mL at 298 K, which was 100 times lower than the solubility of HA in water (101.6 mg/mL) at 298 K. The solubility difference of HA and HAH induced selective precipitation of HAH with dilution of the product solution. The precipitated HAH was separated by filtration to obtain highly pure HAH. After the purification, 11 g of purified HAH were obtained from 10 g HMF in the one-pot conversion giving a 99% yield. Figure 3 shows the NMR spectrum of precipitated HAH. We note that no other chemical shifts from impurities or unreacted reagent were observed, showing that high purity HAH can be produced by filtration purification after the reaction at 308 K.

Kinetic model for aldol condensation of HMF and acetone

The reaction kinetics for aldol condensation of HMF and acetone were investigated at 308 K to measure the rate constants of two step aldol condensation and to determine the time for addition of acid to terminate the condensation reaction (see Figure S11). The rate expressions, described in Equations 6–9, were used to fit the kinetic data shown in Figure 4. In agreement with the literature, all reactions were assumed to be first order in HMF, acetone, and NaOH.[23] We note that we do not take into account the degradation of reactant and product since under our reaction conditions minimal HMF self-condensation and degradation of products were observed. Since, aldol condensation is irreversible in the presence of homogeneous base catalyst, and therefore, only forward rate constants were used in the kinetic model. It should be noted that there is some mismatch between the predictions of kinetic model and the experimental observations at the beginning of the reaction. This discrepancy is because we did not measure the concentration of hydrolyzed intermediates (see Scheme S1) produced during aldol condensation, which were shown to be prominent during the initial phase of reaction.[36] The rate constants of HA production (k_1) and HAH production (k_2) were measured to be 1.59 ± 0.14 ($L^2/mol^2 \cdot min$) and 2.95 ± 0.50 ($L^2/mol^2 \cdot min$), respectively.

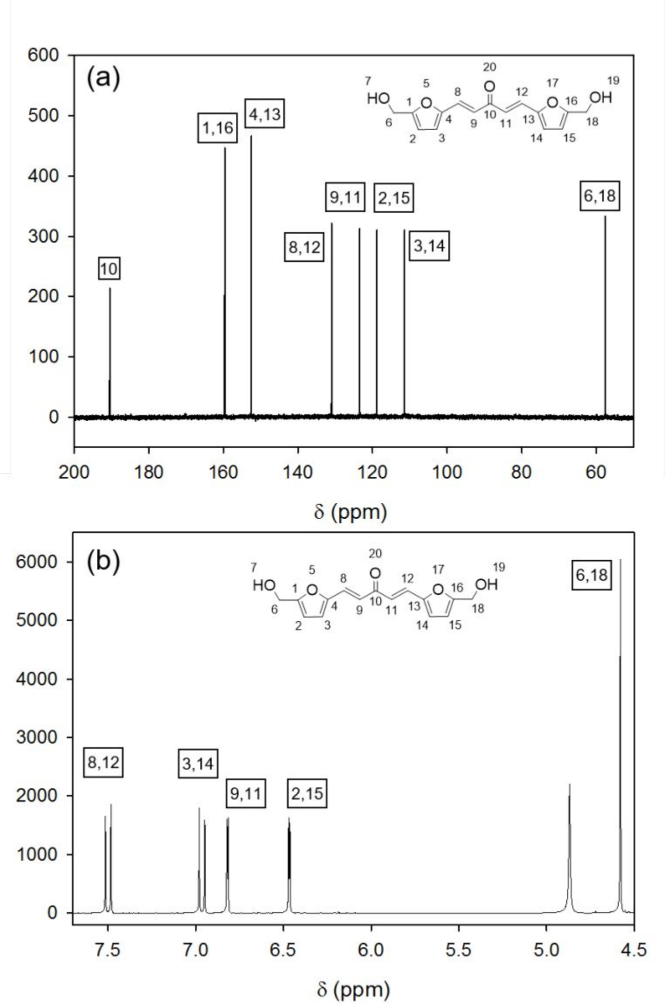


Figure 3. (a) ^{13}C quantitative NMR spectra of purified **2** (HAH) (126 MHz, MeOD) δ: 190.50 (s), 159.66 (s), 152.52 (s), 131.02 (s), 123.43 (s), 118.83 (s), 111.42 (s), 57.62 (s) ppm. (b) ^{1}H standard NMR spectra of purified **2** (HAH) (500 MHz, MeOD) δ: 7.51 (s), 7.48 (s), 6.98 (s), 6.95 (s), 6.82 (d), 6.47 (d), 4.59 (s) ppm (MeOD: 4.87 (s) ppm).

$$\frac{d[HMF]}{dt} = -k_1[NaOH][Ac][HMF] - k_2[NaOH][HA][HMF] \quad (6)$$

$$\frac{d[Ac]}{dt} = -k_1[NaOH][Ac][HMF] \quad (7)$$

$$\frac{d[HA]}{dt} = k_1[NaOH][Ac][HMF] - k_2[NaOH][HA][HMF] \quad (8)$$

$$\frac{d[HAH]}{dt} = k_2[NaOH][HA][HMF] \quad (9)$$

$[HMF]$: concentration of HMF (mol/L), $[Ac]$: concentration of acetone (mol/L), $[NaOH]$: concentration of NaOH (mol/L), $[HA]$: concentration of HA (mol/L), $[HAH]$: concentration of HAH (mol/L), k_1: rate constant of HA production, k_2: rate constant of HAH production, t: reaction time (min).

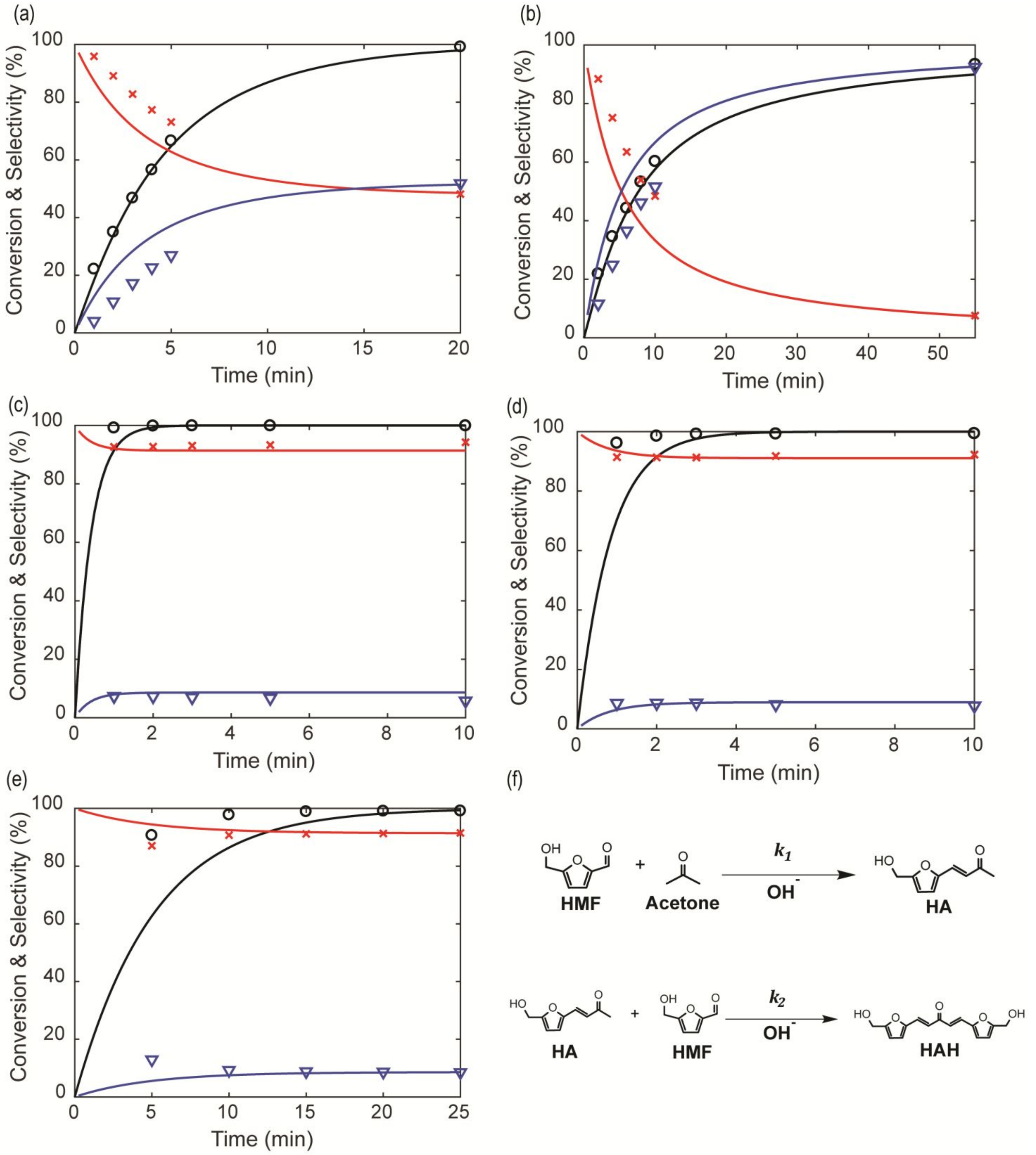


Figure 4. Experimental data and kinetic model (conversion and selectivity trajectories) for aldol condensation of HMF and acetone in batch reactor at 308 K. Solid lines are kinetic model and points describe experimental data (Black: HMF conversion, Red: HA selectivity, Blue: HAH selectivity). Reaction conditions: (a) [NaOH] = 0.10 M, [HMF] = 1.00 M, [Ac] = 1.20 M; (b) [NaOH] = 0.11 M, [HMF] = 1.06 M, [Ac] = 0.53 M; (c) [NaOH] = 0.24 M, [HMF] = 0.61 M, [Ac] = 6.08 M; (d) [NaOH] = 0.12 M, [HMF] = 0.64 M, [Ac] = 6.08 M; (e) [NaOH] = 0.02 M, [HMF] = 0.61 M, [Ac] = 6.07 M. (f) Two step reaction pathways for the base-catalyzed aldol condensation of HMF and acetone.

Hydrogenation of aldol condensed product (HAH)

5 was produced by hydrogenation of HAH over 5 wt% Pd/Al_2O_3 catalyst in 2-propanal/water (80/20 (v/v)) solvent system at 453 K, under 55 bar H_2. Complete conversion of HAH was achieved in 8 hours and the product mixture of both **4** and **5** with the molar ratio of **5** to **4** equal to 5.7 (See Figure S9). We note here that no carbon loss was observed during hydrogenation of HAH. The intermediates (**3**, **4** in Scheme 1) of hydrogenation were synthesized to elucidate hydrogenation mechanism over Pd/Al_2O_3 as well as prepare standards for quantification. By varying the reaction temperature, solvent system, and residence time we were able to selectively produce either **3** or **4**. At 393 K and WHSV of 93 h^{-1}, we selectively synthesized **3** from 4.6 mM HAH in methanol solvent by decreasing hydrogenation rate. Similarly, **4** was selectively produced from 6.4 mM HAH in methanol solvent at 423 K and WHSV = 47 h^{-1} with higher hydrogenation rate. The molecular structure of **3** and **4** were characterized by ^{13}C and ^{1}H NMR (see Figure S2 and S3). The hydrogenation pathways for HAH are described in Scheme 1. Based on the molecular structures of the intermediates we show that first the two unsaturated bonds in the aliphatic chain of HAH molecule were hydrogenated to produce **3**. Next, the furan rings were saturated to produce **4**. Compound **5** was synthesized by complete hydrogenation of double bonds and ketone group in **2**. The central ketone group in the molecular structure of **2** has the lowest activity for hydrogenation (see Scheme 1). The selectivity of **5** increased by changing the solvent system from methanol to 2-propanol/water. The molar ratio of **5** to **4** increased from 1.24 in methanol/water (85/15 (v/v)) solvent system to 5.70 in 2-propanol/water (80/20 (v/v)) which demonstrated higher hydrogenation activity in the 2-propanol/water solvent system.

Hydrodeoxygenation and ring-opening

Recent work on Pt-WO_x/TiO_2 catalysts has shown that this material effectively opens the five membered ring of tetrahydrofuran-dimethanol (THFDM) and was also active for hydrodeoxygenation of the hydroxyl groups due to hydrogen spill-over from Pt to WO_x.[17] **4** and **5** were converted to a mixture of **6** and **7** over Pt-WO_x/TiO_2 catalyst at 383 K, 433 K and 483 K (see Figure 5). We note here that the reaction pressure includes the vapor pressure of the solvent at the reaction temperature. 30 bar H_2 was filled in the reactor initially to begin the reaction. 30 bar H_2 and 383-483 K reaction conditions for hydrodeoxygenation are less severe compared to previous works.[37,38] Figure S6 shows the NMR spectra of the product mixture obtained after hydrodeoxygenation of 5 over Pt-WO_x/TiO_2. It was observed that under our reaction conditions the five membered rings in **5** were opened to produce aliphatic polyol, **6**. Also the ring was opened only at the C_1 and C_{16} position (see Figure 3) due to the steric hindrance. As a result, we selectively produce **6** instead of a mixture of isomers. Additionally, under the reaction condition studied, two terminal hydroxyl groups and one secondary hydroxyl group in **5** were removed by hydrodeoxygenation to produce **7**. These results are consistent with previous work on hydrodeoxygenation of THFDM over Pt-WO_x/TiO_2.[11] The selectivity of **6** and **7** is determined by the kinetics of each reaction. The molar ratio of **6** to **7** decreased from 2.8 to 0.7 with increasing the reaction temperature from 383 K to 433 K (see Figure 5) which implies that the activation energy of hydrodeoxygenation was higher than that of ring-opening. However, the combined yield of **6** and **7** was 90% and 96% at 383 K and 433 K, respectively. Increasing the reaction temperature to 483 K led to loss of product by C-C cleavage and polymerization of products. The combined yield of **6** and **7** was 34% at 483 K (see Figure 5).

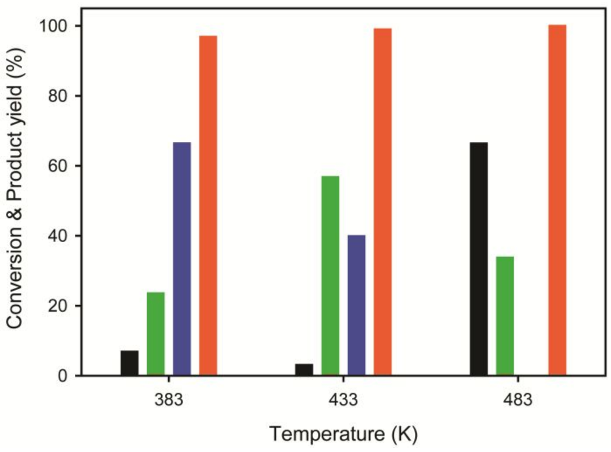


Figure 5. Conversion and Product yield during ring opening and hydrodeoxygenation of **4** and **5** over Pt-WO_x/TiO_2 at different reaction temperatures. Different amount of catalyst and reaction time were used to obtain complete conversion of **4** and **5**. Feed/Catalyst (g/g) = 4.5 was used for 24 h reaction under 56 bar H_2 at 483 K, Feed/Catalyst (g/g) = 2.2 was used for 24 h reaction under 55 bar H_2 at 433 K. Feed/Catalyst (g/g) = 1.2 was used for 60 h reaction under 51 bar H_2 at 383 K (Black: yield of unidentified products, Green: yield of **7**, Blue: yield of **6**, Orange: conversion of **4** and **5**).

Conclusions

We describe a sustainable process to produce biomass-derived high molecular weight chemicals. Various high molecular weight chemicals (>240 g/mol) consisting of 15 carbon atoms were produced in high yield. It was shown that the selectivity to HA and HAH during aldol condensation is easily controlled by regulating the concentrations of acetone and HMF in the feed. However, we observed that the products degrade after completion of aldol condensation in presence of the base catalyst. As such the product solution was neutralized quickly to prevent degradation of condensation products. It was shown that if the product solution is neutralized quickly after completion of the reaction, 99% yield of HAH can be achieved. Additionally, it was shown that highly pure HAH (> 99% purity) can be obtained by simply diluting the product mixture with water leading to spontaneous precipitation of HAH. Moreover, HAH was hydrogenated to **5** over Pd/Al_2O_3 in 2-propanol/water solvent system. We show that solvent system plays an important role during hydrogenation of HAH. Furthermore, **6** and **7** were synthesized from **5** over Pt-WO_x/TiO_2 catalysts by ring-opening and hydrodeoxygenation, respectively. We show that the selectivity towards **6** or **7** can be controlled by changing the reaction temperature. At lower reaction temperature (< 433 K), ring opening is favoured producing **6**; whereas at higher reaction temperature (> 433 K), **7** was selectively produced from **5**. However, we note that above 483 K undesired products are formed due to the C-C cleavage and polymerization of products.

Conflicts of interest

Authors declare no conflict of interest.

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