Supporting Information

One-pot synthesis of 2-hydroxymethyl-5-methylpyrazine from renewable 1,3-dihydroxyacetone

Lei Song, Mingyuan Zheng, Jifeng Pang, Joby Sebastian, Wentao Wang, Minjie Qu, Jian Zhao, Xinhong Wang and Tao Zhang

a Materials Science and Engineering, Dalian Polytechnic University, Dalian, 116034, China. E-mail: qumj@dlpu.edu.cn
b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China. E-mail: myzheng@dicp.ac.cn

1. Experimental Section

1.1 Materials

1,3-dihydroxyacetone (DHA, 99%) was purchased from Sun Chemical Technology (Shanghai) Co., Ltd. Diammonium phosphate (DAP, 99%) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Standard sample of 2-hydroxymethyl-5-methylpyrazine (HMMP) with 98% purity was provided by Beijing InnoChem Science & Technology Co., Ltd. All the other chemicals were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

All chemicals were used as received without any pretreatments.

1.2 Reaction

The conversion of different biomass-derived chemicals was performed in a stainless-steel autoclave. In a typical experiment, 15 mL deionized water, 1.5 mmol feedstock and 3.0 mmol DAP were added to the reactor, which was put in an oil bath at target temperatures under magnetic stirring. The reaction time was recorded as soon as the reactor was put in the oil bath. After the reaction, the liquid product was cooled to room temperature, and filtrated for analysis.

The kinetic measurements were carried out in a stainless-steel reactor equipped with sampling tube and pressure control system. Typically, 30 mL of 13.33 wt% DAP solution with dioxane and water (50:50 v/v) as the solvent was put into the autoclave. Then, the autoclave was heated to the desired temperature (60 °C, 70 °C and 80 °C). DHA at a concentration of 4 wt% was pumped into the reactor by a Shimadzu LC pump (LC-20A) at a flow rate of 10 mL/min. After the feeding
(the initial time, t=0), samples were taken from the reactor at a certain time intervals (60 s, 300±120 s, 600 s, 900 s) for analysis.

1.3 Analytical methods

The conversions of reactants were analyzed using a high-performance liquid chromatography (HPLC, Agilent 1200) equipped with a Shodex Sugar SC1011 column and a differential refractive index detector system. The products were analyzed with a gas chromatograph (GC, Agilent 7890B) equipped with a CP-WAX FFAP CB column and a FID detector.

The reactant conversions were calculated by:

\[
\text{Conversion (\%)} = \frac{\text{moles of carbon in the converted reactant}}{\text{moles of carbon in the feedstock}} \times 100\%
\]

The HMMP yield was calculated by:

\[
\text{Yield (\%)} = \frac{\text{moles of carbon in HMMP}}{\text{moles of carbon in the feedstock}} \times 100\%
\]

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were recorded on Bruker AVANCE III 500 MHz spectrometer.

The attenuated total reflection infrared (ATR-IR) spectra were collected on a BRUKER Equinox 55 spectrometer equipped with liquids retainer and volatiles cover at 363 K.

The products were identified with Gas chromatography–mass spectrometry (GC-MS) (Varian 450-GC, 320-MS) equipped with a Varian CP-WAX58 (FFAP) CB capillary column. ChemStation TM software was used for data acquisition and a NIST Mass Spectral Library software (NIST 08, Software Version: 2.0 f) was used for the sample identification.

2. Results
Fig. S1 GC-MS spectra of typical product after reaction. Reaction conditions: 0.1 mol/L DHA, 0.1 mol/L DAP, 15 mL deionized water, 90 °C, 1 h, protection gas: 0.1 MPa nitrogen.
Fig. S2 $^{13}$CNMR (176 MHz, D$_2$O) spectra of the reaction liquid after reaction 10, 20, 45 and 60 min.

Reaction conditions: 1.5 mmol of DHA and 3.0 mmol of DAP in 15 mL of D$_2$O under magnetic stirring, at 90 °C.

Fig. S3 HPLC chromatograms of the products in the reaction at different time. The reaction was conducted with 1.5 mmol of DHA and 3.0 mmol of DAP in 15 mL of H$_2$O under magnetic stirring at 90 °C. HPLC analysis conditions: Agilent 1200 HPLC, pure water as mobile phase, UV detector at UV 280 nm, Shodex Sugar SC1011 column.
Fig. S4 $^1$HNMR (500 MHz, D$_2$O) and $^{13}$CNMR (126 MHz, D$_2$O) spectra of typical product obtained in this work and the standard sample of HMMP (98%). Reaction conditions: 4.5 mmol of DHA and 9 mmol of DAP in 45 mL of deionized water under magnetic stirring, at 90 °C, 60 min. After the reaction, the products were extracted with 30 mL ethylacetate, and then ethylacetate was evaporated and 0.5 ml of D$_2$O was added for NMR analysis.
$^1$HNMR (500 MHz, D$_2$O) $\delta$ 8.51 – 8.32 (m, 1H), 4.71 (dd, J = 31.0, 6.2 Hz, 1H), 2.49 (d, J = 24.6 Hz, 2H).

$^{13}$CNMR (126 MHz, D$_2$O) $\delta$ 152.99, 151.49, 143.62, 141.27, 61.87, 19.82.

**Fig. S5** Conversion of DHA and yield of HMMP using different ammonium salts. Reaction conditions: the reaction was conducted with 1.5 mmol of DHA and 6.0 mmol of NH$_4^+$ in 15 mL of deionized water under magnetic stirring, at 90 °C, 60 min; The pH of reactant solutions was adjusted to 8-9 with NaOH or HCl.

**Fig. S6** Conversion of DHA and yield of HMMP at different reactant concentrations. Reaction conditions: reactions were conducted with 0.1, 0.2 and 0.4 mol/L DHA and 0.2, 0.4 and 0.8 mol/L DAP in water, respectively, under magnetic stirring, at 90 °C, 60 min.
Fig. S7 Pictures of the product separation by thin-layer chromatography (TLC). Reaction conditions: 1 mol/L of DHA and 1 mol/L of DAP in H₂O at 90 °C, 30 min. Separation conditions: TLC was performed on glass-backed silica gel plates (CH₃OH/CHCl₃ = 1/10 as eluent), λ = 365 nm.

Fig. S8 ¹H NMR (400 MHz, D₂O) spectra of the products (A-G) isolated by thin-layer chromatography after the reaction. Reaction conditions: 1 mol/L of DHA and 1 mol/L of DAP in H₂O at 90 °C, 30 min. NMR analysis: ¹H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard.
Fig. S9 $^1$HNMR (400 MHz, D$_2$O) and $^{13}$CNMR (101 MHz, D$_2$O) spectra of the product (B) isolated by thin-layer chromatography after the reaction. Reaction conditions: 1 mol/L of DHA and 1 mol/L of DAP in H$_2$O at 90 °C, 30 min.

B: $^1$HNMR (400 MHz, D$_2$O) δ 8.48 (2 H, s), 4.74 (1 H, s), 2.53 (2 H, s).

$^{13}$CNMR (101 MHz, D$_2$O) δ 153.80, 153.78, 143.79, 143.18, 62.15, 20.11.
**Fig. S10** The concentration and conversion of DHA and the yield of HMMP at different reaction times. Conditions: reaction at 70 °C in a mixture solvent of dioxane and water (50%:50% v/v).

**Fig. S11** Plots of ln(C₀/C) versus time for DHA conversion (pseudo-first order). Conditions: reaction at 60-80 °C in a mixture solvent of dioxane and water (50%:50% v/v).
Fig. S12 Arrhenius plot and apparent activation energy of DHA conversion to HMMP. Conditions: reaction at 60-80 °C in a mixture solvent of dioxane and water (50%:50% v/v).