# Electronic Supplementary Information for

# Production of cellulosic gasoline via levulinic ester self-condensation

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## 1. Materials

Chemicals were used as received. Ethyl levulinate (EL, 98%) was purchased from Acros. Sodium (98%), octane (98%), nonane (99%), and dodecane (99%) were purchased from Alfa Aesar. Tetradecane (99%), sulfuric acid (98%), and sodium sulfate (98%) were purchased from Sigma-Aldrich. Palladium on alumina (5 wt%, Escat<sup>™</sup> 1241) was purchased from Strem. 1,2-Dimethylcyclohexane (98%) was purchased from TCI. Absolute ethanol was purchased from Koptec. Ethyl acetate and mixed hexanes were purchased form Fischer Scientific. Silica gel was supplied by Fuji Silysia Chemical Ltd.

## 2. Experimental procedures

## 2.1 Base induced self-condensation of ethyl levulinate

Finely divided sodium metal (0.800 g, 34.8 mmol) was carefully added into absolute ethanol (22 mL) and the mixture was stirred at room temperature until the metal dissolved. The resulting sodium ethoxide solution was added dropwise into a stirred mixture of ethyl levulinate (5.00 g, 34.7 mmol) and Na<sub>2</sub>SO<sub>4</sub> (1.50 g) in absolute ethanol (20 mL) under argon. The reaction flask was flushed three times with argon and then heated at 50 °C for 5 h with good stirring, during which the mixture gradually turned orange and a red gel was observed adhering to the wall of the vessel. The reaction was allowed to cool to room temperature and 20 wt% H<sub>2</sub>SO<sub>4</sub> in ethanol was added until the mixture was pH 2. The resulting paste was collected on a filter and washed with ethanol to give a yellow filtrate. The filtrate was diluted with ethanol to a volume of 50 mL and 5 drops of H<sub>2</sub>SO<sub>4</sub> were added. The mixture was heated at 50 °C overnight and then the solvent was evaporated. The residue was partitioned between water and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated to give the crude product (4.30 g) as a yellow-orange oil. The yield of **6** was determined by GC-MS using a sample of 6 as an external standard. The crude product was purified by silica gel chromatography (hexane : ethyl acetate=3:1) to give **6** as a yellow oil (1.77 g, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.22 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.34 - 3.29 (m, 2H), 3.24 (q, J = 2.4 Hz, 2H), 2.32 (t, J = 2.4 Hz, 3H), 2.05 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.9, 165.0, 156.1, 146.7, 134.7, 126.5, 60.8, 59.3, 45.4, 31.4, 14.5, 14.2, 14.2, 13.6. HRMS calcd for C14H20O4 253.1435 [M+H<sup>+</sup>], found 253.1441.

#### 2.2 Hydrogenation of 6 to 7

Compound **6** (0.910 g, 3.61 mmol), 10% Pd/C (180 mg) and ethanol (20.0 mL) were combined in a 300 mL Parr Hastelloy autoclave. The vessel was sealed, flushed with H<sub>2</sub> and then pressurized to 1.2 MPa H<sub>2</sub>. The reaction was conducted at 80 °C for 6 h with good stirring. After cooling to room temperature the catalyst was removed by filtration and the solvent was evaporated to give a colorless oil which was a mixture of the isomers of the **7** (0.850 g, 92%). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  176.1, 176.1, 175.0, 174.6, 173.8, 173.4, 173.2, 173.0, 60.3, 60.2, 60.1, 60.0, 51.4, 51.1, 50.2, 50.0, 47.5, 46.9, 46.5, 46.2, 46.0, 45.1, 43.4, 42.4, 42.2, 42.0, 40.0, 39.9, 39.7, 39.3, 37.8, 37.5, 37.3, 36.7, 36.5, 35.9, 35.5,

34.7, 34.6, 34.6, 34.5, 34.3, 31.3, 19.4, 18.7, 18.4, 18.3, 17.9, 16.2, 16.0, 15.6, 15.3, 14.3, 14.3, 14.2, 14.2, 14.2, 11.8. HRMS calcd for C<sub>14</sub>H<sub>24</sub>O<sub>4</sub> 257.1748 [M+H<sup>+</sup>], found 257.1758.

#### 2.3 Hydrogenation-decarboxylation of 6

Compound **6** (0.798 g, 3.17 mmol), 5% Pd/Al<sub>2</sub>O<sub>3</sub> (162 mg) and tetradecane (10.0 mL) were combined in a 300 mL Parr Hastelloy autoclave. The vessel was sealed, flushed with H<sub>2</sub>, pressurized to 4.0 MPa H<sub>2</sub> and heated at 320 °C for 5 h. After the reaction the autoclave was cooled first to room temperature and then further cooled in an ice bath. The pressure was gently released through a bubbler filled with cold acetone. After opening the reactor, the walls were washed down with acetone and the combined washings and contents of the bubbler was diluted with acetone to a volume of 50 mL for GC-MS analysis (see Section 2.5), which indicated a total hydrocarbon yield of 94%.

#### 2.4 Decarboxylation-hydrodeoxygenation of the crude levulinate ester condensate

Procedure 2.1 for the base induced self-condensation of ethyl levulinate was followed using sodium metal (4.00 g, 174 mmol), ethyl levulinate (25.0 g, 174 mmol), Na<sub>2</sub>SO<sub>4</sub> (10.0 g), and ethanol (150 mL). At the end of the reaction, most of the ethanol was evaporated and the crude product was partitioned between saturated aq NaCl and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and the solvent was evaporated to give a viscous yellow oil (18.6 g).

The crude dimer-trimer mixture (3.50 g) and 5% Pd/Al<sub>2</sub>O<sub>3</sub> (0.704 g) were combined in a 300 mL Parr Hastelloy autoclave. The vessel was sealed, flushed with H<sub>2</sub>, pressurized to 4.0 MPa H<sub>2</sub> and heated at 320 °C for 5 h. After the reaction the autoclave was cooled first to room temperature and then further cooled in an ice bath. The yield of hydrocarbon product was obtained by two different methods: (1) The reaction mixture was transferred into a flask using a pipette and the surfaces of the autoclave were swabbed using a pre-weighed quantity of cotton to collect the remaining product and catalyst. After removal of a small amount of water-ethanol mixture with a pipette, the total yield of hydrocarbon (1.64 g) was determined. The molar yield could be approximated as described in Section 2.5 below, the calculation of which gives a value of 91%. (2) The pressure in the cooled autoclave was gently released through a bubbler filled with cold chloroform. After opening the reactor, the surfaces were washed down with chloroform and the combined washings and contents of the bubbler were dried over solid NaOH. The mass of chloroform and the ethanol by-product were determined by NMR integrations using benzene as internal standard and subtracted from the total mass of the mixture to give the hydrocarbon yield (1.66 g). The molar yield could be approximated as described in Section 2.5, the calculation of which gives a value of 93%.

Two further scale-up reactions were performed as described above with the crude dimer-trimer mixture (15.00 g each) and 5%  $Pd/Al_2O_3$  (1.50 g). After the reaction, the autoclave was cooled to room

temperature and further cooled in an ice bath. The products of both reactions were combined and filtered through a bed of Na<sub>2</sub>SO<sub>4</sub> to remove the catalyst and water for a total mass of 12.7 g of hydrocarbon product. Since no method was applied to wash the product from the reactor surfaces and filter cake, the calculated hydrocarbon yield (83%) is somewhat lower than above. The product was then distilled to determine the boiling point distribution.

The activity of  $Pd/Al_2O_3$  for this reaction was tested three times in succession under the above conditions. The spent catalyst was re-used without any washing or treatment of any kind. The conversion of crude dimer-trimer mixture was at least 95% in the second and third runs.

## 2.5 Product analysis

The hydrocarbon products were analyzed on an Agilent 6890N GC-MS instrument equipped with a VF-5MS column (30.0 m × 250  $\mu$ m × 0.25  $\mu$ m). The following temperature program was used in the analysis: 40 °C (2 min) – 4 °C /min – 125 °C – 20 °C /min – 280 °C. The carrier gas was He with a flow rate of 1.0 mL min<sup>-1</sup> and the split ratio was 1:60. Mass spectra ranging from *m*/*z*=40-350 were obtained using electron impact ionization (EI). For diester derived products, an internal standard method was applied to measure the mass of cyclic C8, C9 and C10 products. 1,2-Dimethylcyclohexane was used as a model to calculate the response factor (R<sub>1</sub>) of the product cycloalkanes against the corresponding normal alkanes. The secondary response factors of the normal alkane standards against dodecane as an internal standard were then calculated to give overall factors R<sub>C8</sub>, R<sub>C9</sub>, R<sub>C10</sub> of the cyclic C8, C9 and C10 hydrocarbons against dodecane, as shown below.

$$R_{1} = \frac{Area \ of \ C8_{cyclo}}{Mass \ of \ C8_{cyclo}} \times \frac{Mass \ of \ C8_{alkane}}{Area \ of \ C8_{alkane}}$$

$$R_{C8} = R_{1} \times \left(\frac{Area \ of \ octane}{Mass \ of \ octane} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right)$$

$$R_{C9} = R_{1} \times \left(\frac{Area \ of \ nonane}{Mass \ of \ nonane} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right)$$

$$R_{C10} = R_{1} \times \left(\frac{Area \ of \ dodecane}{Mass \ of \ decane} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right)$$

Thus, the response factors of cyclic C8, C9 and C10 against dodecane are:

Table S1 Response factors of cyclic C8, C9 and C10 hydrocarbons against dodecane

R <sub>C8</sub>	R <sub>C9</sub>	Rc10
0.4244	0.5022	0.5875

The yields of cyclic C8, C9 and C10 hydrocarbons were calculated using these expressions:

$$Y_{C8} = \frac{\left(\frac{Total \ area \ of \ C8 \ peaks}{R_{C8}} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right) \div 112g/mol}{m_6 \div 252 \ g/mol} \times 100\%$$

$$Y_{C9} = \frac{\left(\frac{Total \ area \ of \ C9 \ peaks}{R_{C9}} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right) \div 126g/mol}{m_6 \div 252 \ g/mol} \times 100\%$$

$$Y_{C10} = \frac{\left(\frac{Total \ area \ of \ C9 \ peaks}{R_{C10}} \times \frac{Mass \ of \ dodecane}{Area \ of \ dodecane}\right) \div 140g/mol}{m_6 \div 252 \ g/mol} \times 100\%$$

For the decarboxylation-hydrodeoxygenation of the crude dimer-trimer mixture, the yield of C8, C9, C10, C12 and C13 products was calculated as follows:

$$Y = \frac{m_{mixed \ hydrocarbons}}{(m_{condensate} \div 287.3 \ g/mol) \times 147.3 \ g/mol} \times 100\%$$

where 287.3 corresponds to the weighted average of the molecular mass of the dimer monoester monoacid and the trimer diester monoacid, which approximates to the composition of the crude dimer-trimer mixture, and 147.3 is the molecular mass of the averaged product ( $C_{10.5}H_{21}$ ).

# 3. Spectra

#### 3.1 NMR spectra

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Varian 400 NMR spectrometer with an operating frequency of 400 MHz and 100 MHz, respectively. The data were processed using MestReNova desktop NMR data processing software (version 11.0.4).





Figure S2. <sup>13</sup>C NMR spectrum of 6



Figure S3. DEPT 135 spectrum of 6



Figure S4 <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy (COSY) of 6



Figure S5 <sup>1</sup>H-<sup>13</sup>C heteronuclear single-quantum correlation spectroscopy (HSQC) of 6



Figure S6. <sup>1</sup>H NMR spectrum of isomers of 7



Figure S7. <sup>13</sup>C NMR spectrum of isomers of 7



Figure S8. <sup>1</sup>H NMR spectrum of EL derived crude oil





Figure S10. <sup>1</sup>H NMR spectrum of hydrogenation products of EL derived crude oil



Figure S11. <sup>13</sup>C NMR spectrum of hydrogenation products of EL derived crude oil

# 3.2 GC-MS spectra



Figure S12. GC-MS spectrum of hydrogenation products from 6



Figure S13. GC-MS spectrum of hydrogenation products from the crude dimer-trimer mixture

## 3.3 Mass spectra

Mass spectra were recorded using a Bruker microTOF-Q instrument (electrospray ionization, positive ion mode). For high resolution mass spectral analysis, samples were analyzed by flow-injection analysis into a Thermo Fisher Scientific LTQ Orbitrap operated in the centroided mode. Samples were injected into a mixture of 50% MeOH/H<sub>2</sub>O and 0.1% formic acid at a flow of 0.2 mL/min. Source parameters were 5.5 kV spray voltage, capillary temperature of 275 °C, and sheath gas setting of 20. Spectral data were acquired at a resolution setting of 100,000 FWHM using the lockmass feature.



Figure S14. ESI mass spectrum of the esterified dimer-trimer mixture.



Figure S15. ESI mass spectrum of 6



Figure S16. ESI mass spectrum of 7

# 4. Computational Details

Ab initio calculations were performed using the Gaussian 09 suite of programs.<sup>1</sup> Structures were optimized and confirmed as local minima by frequency calculations at the B3LYP/6-31+G(d,p) level of theory in the gas phase and then single point GIAO-NMR calculations were performed on the optimized geometries at the mPW1PW91/6-311+G(2d,p) level of theory using the SMD implicit solvation model (scrf) with chloroform and default radii. Computed isotropic shielding tensors were used to scale the predicted chemical shift values using recommended scaling factors in the equation  $\delta$ =(intercept- $\sigma$ )/(-slope).<sup>2</sup> In this equation,  $\delta$  represents the computed chemical shift values (relative to TMS),  $\sigma$  represents the computed isotropic values, and the slope and y-intercept values were obtained from existing scaling factors in the Chemical Shift Repository database.<sup>2</sup>

<sup>1</sup>H <sup>13</sup>C slope: -1.0936 slope: -1.0533 intercept: 31.8018 intercept: 186.5242

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