Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2021

### **Supplemental Material**

### Properties of Bicyclic and Multicyclic Hydrocarbons as Bio-derived Compression Ignition

### Fuels That Can Be Prepared via Efficient and Scalable Routes from Biomass

Lelia Cosimbescu<sup>a</sup>\*, Kristen B. Campbell<sup>a</sup>, Senthil Subramanian<sup>a</sup>, Marie Swita<sup>a</sup>, Naijia Hao<sup>b</sup>,

Cameron M. Moore<sup>b</sup>, Karthikeyan K. Ramasamy<sup>a</sup>, Andrew D. Sutton<sup>b</sup>, Lisa D. Pfefferle<sup>c</sup>, Charles

S. McEnally<sup>c</sup>, Junqing Zhu<sup>c</sup>

<sup>a</sup>Pacific Northwest National Laboratory, Richland, WA 99352

<sup>b</sup>Los Alamos National Laboratory, Los Alamos, NM 87545

°Yale University, New Haven, CT 06520, USA

#### 2,5-hexanedione-derived Products

Synthesis of methylcyclopentenone (MCP) via Aldol condensation of 2,5-hexanedione (HD) in Parr reactor: A saturated solution of Na<sub>2</sub>SO<sub>4</sub> was prepared as follows: 41.84g of Na<sub>2</sub>SO<sub>4</sub> was slowly added to 100mL water at 32-35 °C and stirred until dissolved. A 300 mL Parr reactor was charged with 24.4g of 2,5-hexanedione (0.214 mmol, 1 eq.), 4.54g of K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (0.0214 mmol, 0.1 eq.), 100mL toluene and the saturated Na<sub>2</sub>SO<sub>4</sub> solution. The mixture was degassed by N<sub>2</sub> fill followed by evacuation cycles, three times. A leak test was performed at 500 psi N<sub>2</sub> pressure, to ensure the system is closed. The pressure was released, and the temperature was raised to 180 °C, under vigorous stirring (800 rpm); from the point when the temperature reached close to 180 C, typically 175-175 °C, the mixture was allowed to heat and stir for an additional hour. After 1h of reaction time, the mixture was allowed to cool to room temperature. The crude was analyzed via GC-FID to determine conversion and selectivity, and it showed complete consumption of 2,5-hexanedione, 97.5 % MCP and 1.95% oligomeric species. The resulting mixture was worked-up by liquid-liquid extraction with DCM and water (3x50mL DCM). The DCM phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo to yield 20.0g of brown oil. Pure MCP was isolated by distillation to yield 16.5 g as a light-yellow oil (80.3%). This procedure yielded MCP with great conversion.

Synthesis of oligomeric MCP mixture via modified conditions from above: A 300 mL Parr reactor was charged with 18.7g of 2,5-hexanedione (0.164 mol, 1 eq), 18.9g of tetramethyl guanidine (0.164 mmol, 1 eq.) and 100mL toluene. The mixture was degassed by N<sub>2</sub> fill followed by evacuation cycles, three times. A leak test was performed at 500 psi N<sub>2</sub> pressure, to ensure the system is closed. The pressure was released, and the temperature was raised to 180 C, under vigorous stirring (800 rpm); when the temperature reached close to 180 °C, typically 175-175 °C, the mixture was allowed to heat and stir for an additional hour. After 1h of reaction time, the mixture was allowed to cool to room temperature. The crude was analyzed via GC-FID to determine conversion and selectivity, and it showed the following product profile: 9.5 % 2,5hexanedione, 33.0% % MCP and 57.4 % oligomeric species. The resulting mixture was workedup by liquid-liquid extraction with DCM and water (3x50mL DCM). The DCM phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo to yield 19.5g of brown oil. In this reaction, the focus was the isolation of the heavier oligomeric species, not MCP, so MCP and starting material were removed by distillation. The distillation residue was the product of interest and it was isolated as a dark brown oil in  $\sim 50\%$  yield (10.7g).

Synthesis of oligomeric MCP mixture from HD via scalable NaOH and toluene reflux conditions: In one example, 2,5-hexanedione (200 mL, 1.75 mol, 1eq), NaOH (7 g, 0.175 mol, 0.1 eq), toluene (269 mL), and water (214.8 mL) were mixed in an oven-dried two-neck round

bottom flask and left stirring at reflux for two days. The mixture was then combined with water (50 mL) and extracted with dichloromethane (2x 100 mL). The aqueous layer was neutralized with 1M HCl (2x 15 mL). The organic phase was then washed with a NaCl solution (1x 50 mL, aq) and then dried over sodium sulfate. The mixture was subjected to distillation to remove toluene and MCP, and the residual material was a thick dark residue (125g).

### <sup>1</sup>H NMR of 3-methyl-2-cyclopentenone (MCP) before and after distillation: Clean MCP

peaks are found at 5.93 (s), 2.60 (s), 2.40 (t), and 2.15 (s) ppm. The <sup>1</sup>H NMR before distillation in Figure S1a shows that although the majority of the peaks are due to oligomerization, MCP was present in the product mixture. After distillation (Figure S1b), there is minimal to no MCP and some residual toluene. The distillate shown in Figure S1c is pure MCP. It is important to note that while MCP appears to be a dominant species in the mixture, considering its much lower molecular weight versus the other components, and the fact that <sup>1</sup>H NMR looks at molar concentration, the heavy fractions actually account for about <sup>1</sup>/<sub>2</sub> of the mixture.

<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 5.94 (s, 1.0H), 3.41 (s), 3.29 (s), 2.59 (s, 0.51H), 2.50 (s), 2.47 (s), 2.41 (t, 2.49H), 2.35 (s), 2.31 (s), 2.29-2.14 (m), 2.15 (s, 0.89H), 2.12 (s), 2.02-1.85 (m), 1.69 (s), 1.64 (m), 1.39-0.93 (m).



Figure S1a. <sup>1</sup>H NMR of the HD-derived Aldol/Michael addition products before distillation.

<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 5.95 (s, 1H), 4.05 (m), 3.98 (b, m), 3.51-3.31 (m), 3.16-2.85 (m), 2.59 (s, 1.29H), 2.46, 2.43, 2.38, 2.35, 2.30, 2.25, 2.20, 2.17, 2.14 (s, 0.59H), 2.04-1.85 (m), 1.71-1.50 (m), 1.45-0.94 (m).



**Figure S1b.** <sup>1</sup>H NMR of the HD-derived Aldol/Michael addition mixture products after distillation.



<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 5.92 (s), 2.60 (s), 2.40 (t), 2.15 (s).

Figure S1c. <sup>1</sup>H NMR of pure MCP distillate.

<sup>1</sup>H NMR and <sup>13</sup>C NMR of HD-derived aldol products after hydrotreatment: Figure S2a is the proton NMR of the hydrotreated product from aldol/Michael addition of HD after distillation. The <sup>1</sup>H NMR shows a complex mixture of many species impossible to decipher due to peak overlap. However, the NMR shows the absence of MCP, but the presence of a small amount of reduced products, cyclic cyclopentenes, with various methyl positions. The <sup>13</sup>C NMR is shown in Figure S2b and shows the presence of olefins (>120 ppm) and alcohols (60-70 ppm) within the mixture. Figures S2c and S2d are a <sup>1</sup>H NMR spectra and a <sup>13</sup>C NMR spectra, respectively, taken after extensively drying the same product.

<sup>1</sup>H NMR (500 MHz, cdcl<sub>3</sub>) δ 6.87 (s), 5.29 (s), 4.35 (t), 4.28 (m), 3.75 (t), 3.65 (t), 3.30 (quint), 2.88 (m), 2.75 (m), 2.59 (d), 2.37 (s), 2.27-0.87 (m).



Figure S2a. <sup>1</sup>H NMR of the hydrotreated HD-derived Aldol/Michael addition products.

<sup>13</sup>C NMR (126 MHz, cdcl<sub>3</sub>) δ 147.14, 141.85, 137.65, 135.50, 131.11, 130.61, 129.61, 127.82, 127.39, 124.33, 77.41, 77.16, 76.91, 68.03, 62.71, 48.89, 46.91, 46.58, 44.69, 40.31, 38.64, 36.97, 35.87, 35.62, 35.00, 34.77, 34.63, 33.22, 31.49, 29.52, 25.71, 25.38, 25.23, 24.29, 22.76, 20.78, 20.36, 19.66, 19.02, 18.92, 18.44, 16.61, 14.20, 13.95, 13.84.



Figure S2b. <sup>13</sup>C NMR of the hydrotreated HD-derived Aldol/Michael addition products.

 $^1\mathrm{H}$  NMR (500 MHz, cdcl\_3)  $\delta$  7.26 (s), 6.88 (s), 2.59 (d,b), 2.38 (s), 2.282-2.10 (m), 1.78-0.92 (m,b), 0.00.



**Figure S2c.** <sup>1</sup>H NMR of the hydrotreated HD-derived Aldol/Michael addition products after drying thoroughly.

<sup>13</sup>C NMR (126 MHz, cdcl<sub>3</sub>) δ 147.68, 141.80, 131.06, 130.55, 130.20, 127.80, 127.00, 77.41, 77.17, 76.91, 73.88, 49.42, 46.88, 43.54, 40.29, 38.60, 34.92, 33.19, 30.25, 29.50, 26.98, 26.92, 25.22, 24.26, 23.17, 19.65, 18.94, 18.45, 14.69.



**Figure S2d.** <sup>13</sup>C NMR of the hydrotreated HD-derived Aldol/Michael addition products after drying thoroughly.

**GC-MS Spectra for HD-derived products before and after hydrotreatment:** Figure S3a is an overlay of the HD-derived products before hydrotreatment (black) and after hydrotreatment (red). Another GC-MS spectra was obtained after extensive drying of this same product shown in Figure S3b.



**Figure S3a**. GC-MS overlay spectra of HD-derived products of the aldol/Michael additions before hydrotreatment (black) and after hydrotreatment (red). Retention time is on the x-axis and the abundance is found on the y-axis.



**Figure S3b**. GC-MS overlay spectra of HD-derived products of the aldol/Michael additions before hydrotreatment (black) and after hydrotreatment (red) extensively dried. Retention time is on the x-axis and the abundance is found on the y-axis.



GPC Data of HD-derived aldol products after hydrotreatment:

Figure S4. GPC data for HD-derived aldol products.



Figure S5. GPC data for HD-derived HDO products.

# **Cyclopentanone-derived Products**

Synthesis of Cyclopentanone-derived Aldol product mixture: In one example,

cyclopentanone (100 mL, 118 mmol, 1 eq.) and 10 % wt. aqueous NaOH (15 mL, 3.75 mmol, 0.03 eq.) were mixed in an oven-dried two-neck round bottom flask and left stirring at light reflux for two days. Then the mixture was combined with water (50 mL) and extracted with dichloromethane (2x 100 mL). To ensure the aqueous layer was neutralized, HCl (2x 5-10 mL,

1M) was added. Next, the organic phase was washed (1x 50 mL) with saturated NaCl (aq) and filtered through celite. Lastly, the organic phase was concentrated, and 79.79 g of oil were recovered. <sup>1</sup>HNMR indicated about 96% conversion based on starting material peaks ratio to the product peaks.

### <sup>1</sup>HNMR of Cyclopentanone aldol product before and after distillation: Cyclopentanone

peaks are found at 2.17 (t) and 1.97 (quin) ppm. Figure S4a, before distillation, shows about an 81% conversion of cyclopentanone to its dimer/trimer product. The disappearance of the cyclopentanone peaks after distillation is evident in Figure S4b, with cyclopentanone only distillate in Figure S4c.

 $^1H$  NMR (500 MHz, cdcl<sub>3</sub>)  $\delta$  2.79 (b, s), 2.54 (m), 2.32 (s), 2.3-2.29 (m), 2.17 (t, 1.00H) , 1.96 (t, 0.70), 1.93-1.89 (m), 1.73-1.67 (m).



Figure S6a. <sup>1</sup>H NMR of the cyclopentanone-derived aldol products before distillation.

<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 2.88 (b, m), 2.79 (b, s), 2.54 (b, s), 2.29 (t), 2.17 (b, t, 1.00H), 1.92 (t), 1.72 (q), 1.59 (b, m).



Figure S6b. <sup>1</sup>H NMR of the cyclopentanone-derived aldol products after distillation.





Figure S6c. <sup>1</sup>H NMR of cyclopentanone distillate.

<sup>1</sup>HNMR and <sup>13</sup>CNMR of cyclopentanone products after hydrotreatment: Figure S5a is the proton NMR of the hydrotreated cyclopentanone aldol condensation product. The <sup>1</sup>H NMR shows mainly the presence of dimer, but also other minor species (trimer). The <sup>13</sup>C NMR is shown in Figure S5b displaying only hydrocarbons and confirming the complete reduction of the mixture (20-54 ppm).



Figure S7a. <sup>1</sup>H NMR of the hydrotreated cyclopentanone-derived aldol condensation products.



<sup>13</sup>C NMR (126 MHz, cdcl<sub>3</sub>) δ 221.26, 137.82, 78.68, 77.16, 54.21, 54.00, 53.14, 46.53, 40.14,

Figure S7b. <sup>13</sup>C NMR of the hydrotreated cyclopentanone-derived aldol condensation products.



**Figure S8**. GC-MS overlay spectra of cyclopentanone-derived products of the aldol condensation before hydrotreatment (black) and after hydrotreatment (red). Retention time is on the x-axis and the abundance is found on the y-axis.

### **Cyclohexanone-derived Products**

**Synthesis of Cyclohexanone-derived Aldol Product**: In one example, cyclohexanone (50 mL, 48.2 mmol, 1 eq.) and sulfamic acid (4.684 g, 4.82 mmol, 0.1 eq.) were combined in an ovendried two-neck round bottom flask and left stirring at reflux (100 °C) for two days. Then the mixture was combined with water (50 mL) and extracted with dichloromethane (2x 80-90 mL). Next, the organic phase was washed (1x 50 mL) with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Lastly, the organic phase was concentrated to recover 39.36 g of oil. <sup>1</sup>HNMR indicated about 75% yield based on conversion of starting material, although this was a crude estimation due to severe overlap of starting materials and product peaks. The compound was purified by distillation to remove starting material.

# <sup>1</sup>HNMR of Cyclohexanone Aldol product before and after distillation: Clean cyclohexanone

peaks are found at: 2.33 (t), 1.87 (q), and 1.72 (m) ppm. Before distillation spectrum shows cyclohexanone peaks, in Figure S7a. In Figure S7b, after distillation spectrum, the cyclohexanone starting material peaks are small (~ 6%) confirming the removal of the bulk of cyclohexanone. in the cyclohexanone spectrum is also shown in Figure S7c, for reference.

<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 3.02 (b, t), 2.90-2.87 (q), 2.57 (b, s), 2.50 (t), 2.41-2.38 (m), 2.34 (t, 1.00H), 2.30-2.27 (m), 2.209 (b, m), 2.04 (b, m), 1.92 (b, s), 1.86 (quint, 1.38H), 1.81 (s), 1.78 (b, d), 1.72 (q, 0.72H), 1.70-1.53 (m).



Figure S9a. <sup>1</sup>H NMR of cyclohexanone-derived aldol products before distillation.

<sup>1</sup>H NMR (499 MHz, cdcl<sub>3</sub>) δ 3.02 (b, t), 2.92-2.88 (m), 2.57 (b, s), 2.50 (t), 2.41-2.39 (m), 2.34 (b, t, 1.00H), 2.30-2.27 (m), 2.20 (b, m), 2.04 (b, m), 1.92 (b, s), 1.86 (quint, 2.15H), 1.84-1.74 (m), 1.72 (q, 3.08H), 1.70-1.53 (m).



Figure S9b. <sup>1</sup>H NMR of the cyclohexanone-derived aldol products after distillation.



 $^{1}\text{H}$  NMR (499 MHz, cdcl<sub>3</sub>)  $\delta$  2.33 (t), 1.87 (quint), 1.73 (q).  $^{55367-77-F1-1H-CDCl3}$ 

Figure S9c. <sup>1</sup>H NMR of pure cyclohexanone distillate.

<sup>1</sup>HNMR and <sup>13</sup>CNMR of cyclohexanone products after hydrotreatment: Figure S8a is the proton NMR of the hydrotreated cyclohexanone-derived aldol condensation mixture. The <sup>1</sup>H NMR detects bicyclohexane (major) and tricyclohexane (minor), a small amount of oxygenates species (peaks between 3-4.5ppm) and small amounts of olefins (peaks between 5 and 6ppm). The <sup>13</sup>C NMR is shown in Figure S8b displaying all the cyclohexanone-aldol products reduced near completion (26-50 ppm).



Figure S10a. <sup>1</sup>H NMR of the hydrotreated cyclohexanone-derived aldol condensation products.





Figure S10b. <sup>13</sup>C NMR of the hydrotreated cyclohexanone-derived aldol condensation products.



**Figure S11**. GC-MS overlay spectra of cyclohexanone-derived aldol products before hydrotreatment (black) and after hydrotreatment (red). Retention time is on the x-axis and the abundance is found on the y-axis.

# **Uncertainty for NSC Calculations**

The uncertainty of the reported NSCs is estimated to be  $\pm$  0.04 based on 2 standard deviations of 7 repeated measurements of the HD-HDO fuels.



Figure S12. Normalized LSSR of HD-HDO-doped flames with different liquid flow rates.

To test whether the liquid fuels were vaporizing completely and were in adsorption/desorption equilibrium with the fuel lines, LSSR signals were measured for the least volatile fuel in this study, HD-HDO, as a function of its dopant flowrate. The results (Figure S10), show a linear relationship between soot concentration and dopant flowrate, which demonstrates that all the injected liquid is reaching the flame.

**Table S1.** Hydrocarbon recovery of the HYD-HDO products. These examples are scale-up runs, and do not necessarily match those examples described above.

| Starting | Th    | Actual       | Aldol | HDO      | Oxygenate       | Weight            | Th yield | Actual | Percent |
|----------|-------|--------------|-------|----------|-----------------|-------------------|----------|--------|---------|
| material | Yd    | yield after  | %     | starting | from            | loss              | after    | yield  | yield   |
|          | after | distillation | yield | weight   | elemental       | due to            | HYD-     | (g)    | (%)     |
|          | Aldol | of SM        |       |          | analysis        | oxygen            | HDO      |        |         |
|          |       |              |       |          | (wt%)           | loss <sup>a</sup> | (g)      |        |         |
|          |       |              |       |          |                 | (g)               |          |        |         |
| Ch       | 163   | 117.5        | 72    | 117      | 11.2            | 11.98             | 105      | 84.7   | 80.6    |
| (200g)   |       |              |       |          |                 |                   |          |        |         |
| Ср       | 151.7 | 124.3        | 82    | 106.6    | 9.7             | 11.39             | 95.2     | 71.2   | 74.8    |
| (193g)   |       |              |       |          |                 |                   |          |        |         |
| HD       | 168.5 | 133.5        | 80    | 133      | ND <sup>b</sup> | ND                | ND       | 100.97 | ND      |
| (200g)   |       |              |       |          |                 |                   |          |        |         |

<sup>a</sup> HYD-HDO results in one mole of [O] lost per mole of compound; the value is estimated based on major component, difficult to determine exact amount, due to mixture profile. <sup>b</sup> The HD aldol product was very viscous and had to be dissolved in THF and DCM for EA analysis, and % oxygen is artificially much higher; therefore, a value could not be estimated.