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Properties of Bicyclic and Multicyclic Hydrocarbons as Bio-derived Compression Ignition Fuels That Can Be Prepared via Efficient and Scalable Routes from Biomass

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Abstract

A series of multicyclic hydrocarbons were synthesized in high yield and under mild conditions from 2,5-hexanedione, cyclohexanone and cyclopentanone, at scales of 200 g. Aldol products were obtained with conversions of 95% (2,5-hexanedione), 80-90% (cyclopentanone) and 75-80% (cyclohexanone), based on the consumption of starting materials. Cyclopentanone and cyclohexanone aldol condensations resulted in mixtures containing mainly the bicyclic products (90%) as well as tricyclic analogs (<10%). The 2,5-hexanedione aldol condensation produced 50% methylcyclopentenone (MCP) as expected and about 50% oligomers. Surprisingly, the complex heavy fraction after removal of MCP contained mainly products of Michael addition of MCP and only a minor fraction of self-aldol condensation product of MCP. The hydrogenation-hydrodeoxygenation (HDO) of cyclohexanone- and cyclopentanone-derived reactants under nickel on alumina (Ni-Al_2O_3) catalyst at 250 °C and pressures between 800 to 1200 psig, produced the expected saturated hydrocarbons with good recovery (80% and 76% respectively), with only small amounts of oxygenated residual starting materials remaining (<2%). However, the HDO of the 2,5-hexanedione aldol mixture produced an equally complex mixture compared

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to its respective aldol/Michael addition product which contained unreacted oxygenates. All crude mixtures, only treated to remove water after HDO unless stated otherwise, were evaluated for their properties as potential compression-ignition fuels: distillation curve, derived cetane number, sooting tendency, lower heating value, density, flash point and cold flow properties. The results show the utility of these hydrocarbons as viable compression-ignition fuels or blendstocks, particularly the cyclopentanone- or cyclohexanone-derived products, or as components of the same.

Keywords: 2,5-hexanedione, bicyclopentane, bicyclohexane, cyclic aldol products, ring-strained fuels, multicyclic hydrocarbons, diesel fuels, jet fuel, derived cetane number, sooting tendency

Introduction

The increase in global oil consumption and demand, and finite fossil-fuel reserves, have fueled the continued development of technologies to manufacture chemicals and fuels from non-petroleum sources of carbon. Lignocellulosic biomass, sustainable, abundant, and environmentally beneficial, is widely used to produce biofuels and other high-value chemicals through different pathways, including biological, thermal and chemical processes. To effectively utilize this massive resource, however, methodologies which are scalable, inexpensive and produce high yields, are necessary for such processes to be competitive with traditional petroleum products, and potentially be adopted. The Co-Optimization of Fuels and Engines Initiative (Co-Optima) is a major collaboration of several national laboratories operated for the U.S. Department of Energy aimed at the co-development of highly efficient engines and fuels/fuel blendstocks. In this context, the main goal of this work is to develop methods to produce multi-gram quantities of promising biomass-derived hydrocarbons suitable for mixing-controlled compression-ignition (MCCI) and diesel fuels as blendstocks.

Compared with straight chain alkanes, cyclic hydrocarbons (especially the strained polycyclic hydrocarbons) have typically higher energy densities and volumetric heating values due to ring strain[1,2,3], which makes them good candidates for transportation fuels. The quest for multicyclic bioderived products has fueled a lot of research in this area towards either catalyst development or new routes for novel bi-and multi-cyclic analogs, mainly due to their promising applications as jet fuel[4,5,6,7]. Similar attributes are potential opportunities to be exploited for diesel blendstocks, which makes this area of research even more attractive, and synergistic with the Co-Optima overarching goal.

A platform molecule which received much attention in the recent years is 5-hydroxymethylfurfural (HMF), which is produced via dehydration of glucose, fructose or sucrose. Reduction of HMF to 2,5-bis(hydroxymethyl)furan, followed by hydrogenolysis or deoxygenation (>95% yield), produces 2,5-dimethylfuran (DMF).[8,9] After DMF is made, its hydrothermal hydrolysis yields 2,5-hexanedione (HD) quantitatively, making this molecule a readily accessible bio-based starting material.[10,11] In an effort to generate multicyclic hydrocarbons from this starting material, various coupling chemistries and subsequent catalysts for hydrodeoxygenation have been explored.[12,13,14,15]

Our starting point was a known route to produce a gasoline additive from HD that involved base-catalyzed,[16,17,18] intramolecular aldol condensation to produce 3-methylcyclopent-2-enone (MCP) as an intermediate. [19,20] MCP was expected to provide a valuable product for gasoline applications, though its partial hydrogenation to 3-methylcylopentanol yielded a high viscosity product unsuitable for gasoline. Nonetheless, full hydrodeoxygenation of MCP produces methylcyclopentane, which is indeed promising, owing to its reported heat of combustion (HHV – higher heating value) of 46.8 MJ/kg. [21,22] However, for a diesel range component, neither product is suitable, as they have a low cetane number despite their high energy density. One of the goals of this work is to develop a method to utilize HD as a biomass-derived platform molecule for the production of diesel-range products with high selectivity using heterogeneous catalysts. The work performed by Sacia et al.[19] provided a path for one of our research targets. They reported that NaOH and KOH base catalysts only provide low yields of MCP. They identified a reaction system for the synthesis of MCP in high yield: saturated aqueous Na_2SO_4 solution, toluene, HD, and K_3PO_4 (3 mol %) heated at 180 °C, for 1h, with the caveat that the chemistry was demonstrated at only 1.2mmol of HD scale. A suitable diesel fuel mixture would have high density, low sooting index and a broad boiling point range above 190 °C, which could only be generated via oligomers that would span a broad boiling range. *Therefore, we aimed at the formation of multicyclic species, not just MCP, resulting from the aldol and Michael addition products of MCP and HD.*

Another platform chemical, readily available from bioderived furfural[23] and produced at industrial scale, is cyclopentanone. Due to its cyclic structure, it too can be used as a feedstock for the synthesis of high-density polycyclic diesel fuels and therefore it became a starting material of interest. An excellent review by Muldoon et.al. describes many efforts in the field of synthesis of multicyclic hydrocarbons and respective catalyst development.[24] Yang et. al. demonstrated the one-step synthesis of the bicyclic C10 hydrocarbon, bicyclopentane, by the combination of self-condensation of cyclopentanone and one-step hydrodeoxygenation (HDO) under solvent-free conditions.[25] Their work explored the efficiency of various solid catalysts to affect the transformation. Others investigated the mixed aldol condensation products of cyclopentanone and furfural. Wang et.al[26] showed one-pot aldol condensation/hydrogenation, and HDO in solvent-free conditions, however full deoxygenation cleaved the furfural ring, so the product was only a monocyclic alkane. Despite the high yield, the process was only shown on 1g scale, so this approach appeared unsuitable for us due to the high-volume requirement for the fuel property analysis. Deng et.al showed a similar approach on slightly larger scales (0.1mol) with good conversions for both cyclopentanone and cyclohexanone in condensation with furfural.[27] Consistent with previous studies, the hydrodeoxygenated final product was monocyclic. Spirocycloalkanes have also been lauded as good potential high-density fuels, due to their bicyclic structure[28]. Spirocycloalkanes are formed by the reductive coupling of cyclic ketones (cyclopentanone, cyclohexanone) and hydrolysis into pinacols, which then rearrange to into spiroketones in the presence of acid catalysts, followed by the Wolff–Kishner–Huang reduction to form the bicyclic alkane. The authors report that under optimal conditions, the overall yields of spiro[5,6]dodecane and spiro[4,5]decane are 52.0% and 64.7%, respectively. Although an interesting route and approach to high density fuels, the reaction steps involve many environmentally unfriendly reagents as well as many purifications and separations, making this a challenging process. Another cyclic ketone of interest is cyclohexanone which can be produced efficiently from lignocellulosic biomass (phenol, phenol ethers), via a concerted catalysis of Pd/C and a Lewis acid.[29,30,31] One of the best works reported so far, in terms of scale and selectivity of monosubstituted products formation, employs phosphotungstic acid encapsulated by a chromium containing MOF, MIL-101. The chemistry was demonstrated at 30g scale which appeared promising.[32] However, the selectivity in the case of cyclohexanone for mono-substitution (95%) was undesirable for our purpose, as we targeted broad boiling point ranges, and the conversion was relatively low at 46%.

Inspired by the body of research mentioned, aside from MCP oligomers, we targeted cyclopentane and cyclohexane dimers and trimers obtained via self-aldol condensations of respective cyclopentanone and cyclohexanone, followed by hydrodeoxygenation. Most of the mentioned literature focuses on catalyst development, selectivity and conversion, but not on providing a scalable process, such that, these methodologies are often demonstrated at sub-gram scale. In contrast, we aimed to produce cyclic hydrocarbons via simple methods that are scalable, inexpensive, robust, and can be easily adopted by industry. The final products and intermediates intentionally did not undergo rigorous purifications/distillations, to streamline the process and probe for the tolerance of the final products to small residual amounts of oxygenates which may be present in an industrial process. Additionally, the materials obtained as a result of hydrodeoxygenation were expected to have high boiling ranges, high LHVs and high cetane numbers to meet diesel fuel specifications among other attributes.

Experimental

Materials: Cyclopentanone, cyclohexanone, 2,5-hexanedione, sulfamic acid, lithium hydroxide, potassium sulfate monohydrate ($K_3PO_4 \cdot H_2O$), polyethylene glycol 300 (PEG300), potassium carbonate, ruthenium trichloride hydrate ($RuCl_3$ xH_2O), tetramethyl guanidine (TMG), sodium iodide (NaI), trimethylsilyl chloride (TMSCl), cetyltrimethylammonium bromide (CTAB), were purchased from Sigma Aldrich and used without further purification. Reagents such as toluene, dichloromethane (DCM), acetonitrile, acetone, hexanes, tetrahydrofuran (THF), sodium chloride (NaCl), sodium hydroxide (NaOH), concentrated hydrochloric acid (HCl) were purchased from Fisher and used as received.

Synthesis of Aldol Products: All reactions were performed in regular glassware without drying, as water was a reagent in the chemical transformation or a product. Mixtures were stirred via magnetic stir bar and heated at or near reflux (100-115 °C). Post-reaction mixtures were neutralized with either 2M NaOH or 2M HCl aqueous solutions, depending on whether an acidic or basic catalyst was employed. The organics were isolated by extraction with DCM, followed by drying with brine and concentration of the mixture under reduced pressure (rotovap). The dimer or oligomer mixtures were separated from starting materials, by vacuum distillation at temperatures below 100 °C. The residual liquid left after distilling low boiling fractions was considered "aldol product"; the removal of starting materials was confirmed via ^{1}HNMR (spectra are provided in the Supplemental Information, Figures S1, S2, S3). Experimental details for each reaction can be found in the supporting information. Conversions were estimated via ^{1}HNMR by integrating starting material peaks versus all product peaks, or in the absence of starting materials, a product profile (mol %) was determined. Product yields (in grams) were reported only for scale-up reactions where aldol products were isolated; theoretical yields were calculated from the weight of the starting material minus the weight of the same moles of water, assuming each condensation formed one equivalent of water. Calculating the theoretical yield via traditional means is not possible, particularly for the MCP oligomer mixture since there is not one major component, but rather a complex mixture with a wide variety of molecular weight components. The cyclopentanone and cyclohexanone products, although made-up of a major fraction (dimer) they also contain small amounts of trimer, so % yield was estimated as just described.

Spectral Characterization: Nuclear magnetic resonance (NMR) spectra were obtained using an NMR system made up of an Agilent DD2 console with an Oxford shielded 51 mm 11.74 T spectrometer at the following frequencies: 500 MHz (^{1}H) and 125.7 MHz (^{13}C{^{1}H}). The chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane (TMS). Samples were prepared in deuterated chloroform, $CDCl_3$. ^{1}HNMR was used to evaluate reaction conversions by integrating starting material peaks versus products. It is important to note that ^{1}HNMR integrations reveal molar ratios of components, not weight ratios, so ^{1}HNMR-derived conversions reflect mol% (mol product/mol of starting material and product). ^{13}CNMR of final post-hydrotreatment mixture were employed to identify the extent of hydrodeoxygenation by monitoring the presence of functional groups such as ketone (180-200ppm), olefin (120-140ppm), and alcohol (60-75ppm).

Hydrodeoxygenation-Hydrogenation: Hydrodeoxygenation-Hydrogenation (HDO) or hydrotreatment experiments were carried out in a continuous fixed-bed, down-flow reactor arrangement. The process flow diagram of the experimental setup is shown in Figure 1. The aldol product liquid feed was metered using a high-pressure liquid chromatography (HPLC) pump and the flow of hydrogen (H_2) carrier gas was metered using a mass flow controller. Both the aldol product liquid and H_2 were fed into a stainless steel fixed-bed reactor with 0.305-inch inner diameter and 0.375-inch outer diameter) stainless steel fixed-bed reactor. The reactor was loaded with 4 g of Engelhard Ni-0750[33], a high-surface-area (145 m2/g) nickel (48%) on γ-alumina, in the middle of the reactor tube in an isothermal zone and the reactor was heated using a band heater to the desired reaction temperature. Prior to loading, the catalyst was sized between 40-60 mesh to attain uniform packing and heating. A thermocouple was placed on top of the catalyst bed to measure the internal reaction temperature. The product stream from the reactor was passed through one of the two cooled (4 °C) sampling condensers where the liquid products were separated from the gases. A back-pressure regulator was used to maintain the desired reactor operating pressure. Samples were collected and analyzed every 24 hrs. A gas flow meter located downstream of the back-pressure regulator was used to continuously monitor the product gas flow rate. A small portion of the product gas was diverted to an Agilent four-column micro gas chromatograph (μGC) with a thermal conductivity detector (TCD) to analyze the permanent gases and the low molecular weight hydrocarbons, to monitor the decarboxylation and cracking products. The experiments were conducted at temperatures between 250 °C and 300 °C, at pressures between 800 to 1200 psig, with a weight hourly space velocity (WHSV) of 0.5 h^{-1} and a H_2 flow of 50 ml/min.

Preliminary experiments utilized Pd/C and Pd-Re/C catalysts which were prepared as follows: DI water was added to appropriate metal solutions according to the calculated pore volume of the carbon support for the desired metals concentration. Palladium (II) Nitrate (12.3% w/w) and perrhenic acid (35.84% w/w) were used as precursors for Pd and Re respectively. Based on the desired catalyst composition, the metal solution was prepared and added dropwise (4 to 5 drops) over the catalyst support and mixed thoroughly via shaker; the procedure was repeated to achieve uniform wetness over the catalyst surface. The catalyst was then dried overnight at 90 °C. Prior to adding the hydrotreating substrate, the catalyst was reduced under 5% H_2, ramping to 300 °C at 2 C/min and holding for 4 hours.

The HDO product contains water, so it was dried for further testing by treating with brine. The organic layer was separated from the aqueous, dried over $MgSO_4$ and filtered through celite and glass wool to remove small solid particles as well as further dry the final product. The HD-derived hydrotreated product contained butane, butanol, and THF and it was dried at 50 °C under vacuum to remove these volatiles before analysis. Some analyses are reported for both "crude" sample (HD-HDO) as well as the dried sample (HD-HDO*). During vacuum drying, other volatile compounds might have been unintentionally removed, aside from THF and butane. The other hydrotreated samples are denoted as Ch-HDO and Cp-HDO.

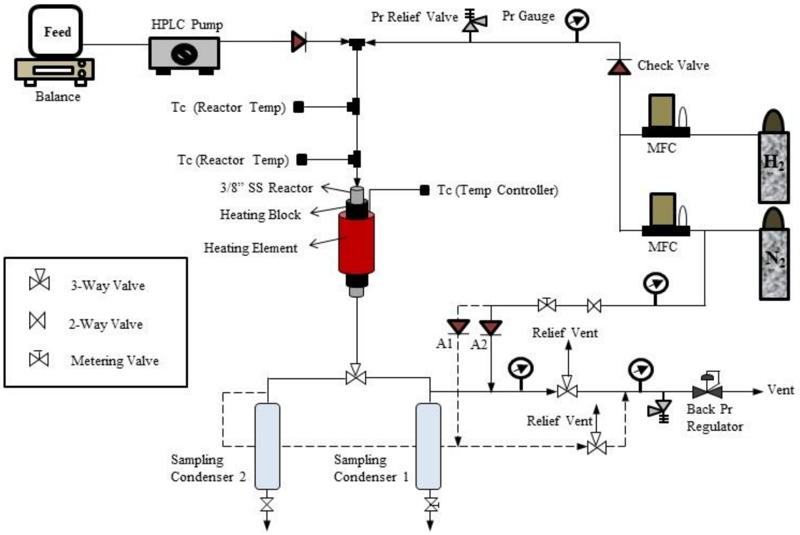


Figure 1. Process flow diagram of the experimental unit used for the Hydrodeoxygenation-hydrogenation (HDO-HYD) chemistry.

Simulated Distillation (SimDist)

Simulated distillation samples were analyzed using an Agilent 6890N gas chromatograph (GC) equipped with a flame ionization detector (FID) and an AC Analytical direct injection programmable temperature injector, cooled with compressed air at 40 psi. The column used was an SGE Analytical Science BPX1 column, 6 m x 0.53 mm and 2.65 µm film thickness. Sample analysis is based on ASTM Method D2887. The GC is calibrated using a standard mixture of *n*-alkanes (*n*-paraffins) from C5 to C44. The retention times of the *n*-paraffins are calibrated with respect to their reported boiling point in °C. The simulated distillation software used was AC Analytical Controls Inc., Revision 6.6. The simulation distillation software integrates the chromatograms by area slices rather than peak integration. The area slices are quantified for mass % with respect to the total area summation of the chromatogram. Samples are always run against both a #2 diesel and a kerosene, along with other QC checks.

Lower Heating Value of mixtures (LHV)

Combustion calorimetry was performed using an IKA C1 compact combustion calorimeter. The calorimeter was calibrated prior to sample measurement using a benzoic acid standard. Higher heating values were measured in triplicate using approximately 0.3 g of sample and averaged, then the contribution due to hydrogen content (determined by elemental analysis) was subtracted to provide the lower heating value (LHV).

Flashpoint measurement

Flashpoint of the diesel fuel candidates were measured using the flashpoint analyzer (Miniflash FPH Vision, AMETEK, Inc.). In each run, 1 mL of the sample was injected into the sample cup and the standard method ASTM D6450 was followed. The ignition interval was defined with 1 °C and the heating rate was defined with 5.5 °C/min. The initial temperature (Ti) and final temperature (Tf) were set to 20 °C and 100 °C, respectively.

Cold flow property measurement

Cold flow properties were measured using a phase analyzer, PSA-70Xi, Phase Technology. In each run, the sample cup was rinsed twice with the sample to be tested. Then 0.15 mL of the sample was injected into the cup. The standard method ASTM D5972 was followed.

Derived Cetane Number (DCN)

All fuel sample DCNs were obtained according to ASTM Method D6890, and measurements were performed at Southwest Research Institute (San Antonio, TX).

Gas Chromatography - Mass Spectrometry Analysis (GC-MS)

Samples were analyzed using an Agilent 5795C GCMS. The column was an Agilent HP-5MS 30m x 0.25mm x 0.25um film thickness with a carrier gas of helium at 0.8mL/min. Oven temperature was initially held for 1 min at 30 °C, ramped at 6 °C/min with a final temperature of 300 °C. Final oven hold of 2 minutes was used. The inlet was heated at 250 °C and 1uL of sample was injected using a split injection of 100:1.

The GC-MS of each aldol and respective hydrotreated product were overlapped and are shown in the SI: HD - Figure S3a/S3b; Cp – Figure S8; Ch – Figure S11. The GC-MS of each individual product was evaluated, and major peaks identified based on suggested compounds by the GC-Database, or by comparing with excepted m/z for the theoretical compounds. The assignments were based on molecular ions and not on published EI spectra of known compounds.

Gas Chromatography via Flame Ionization Detection Analysis (GC-FID)

Samples were analyzed using an Agilent 6890GC equipped with a flame ionizing detector. The column was an Agilent HP-5MS 30m x 0.25mm x 1.0um film thickness with a carrier gas of helium at 2.0mL/min. Oven temperature was initially held for 1 min at 40°C, ramped at 10°C/min with a final temperature of 325°C. Final oven hold of 10 minutes was used. The inlet was heated at 260 °C and 1uL of sample was injected splitless. The samples that were very viscous were diluted with THF prior to analysis (HD-aldol and HD-HDO).

Elemental analysis CHNS

Neat samples were analyzed using an Elementar Vario Macro Cube. Combustion and reduction tubes were packed accordingly to analyze carbon, nitrogen, sulfur, and hydrogen. The combustion tube was heated to 1150 °C and the reduction tube to 850 °C. Helium was used as the carrier gas. This analysis provided %H in the sample.

Sooting Tendency

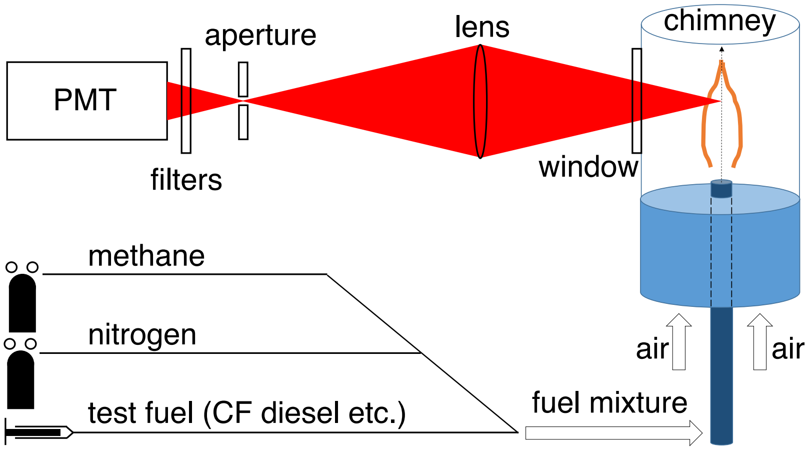


Figure 2. A schematic diagram of the experimental apparatus for measuring sooting tendency.

Sooting tendencies were measured using a yield-based approach similar to a method developed earlier by McEnally et al. [34]. Figure 2 shows the apparatus that was used and McEnally et al. [35] . An emissions-certification diesel fuel from Chevron-Phillips Chemical Co., denoted “CF diesel”, was used as a reference; Mueller et al. [36] describes its composition and properties. The measurements consisted of three steps: (1) sequentially doping the CF diesel and each test fuel into the fuel of a methane/air non-premixed flame at a liquid-phase flowrate of 50 µl/h; (2) measuring the maximum soot concentration in each flame with line-of-sight spectral radiance (LSSR); and (3) normalizing the signals into a normalized soot concentration (NSC) for each test fuel defined by:

$$NSC = \frac{LSSR_{TF} - LSSR_{UD}}{LSSR_{CF} - LSSR_{UD}} \qquad (1)$$

where the subscripts TF, CF, and UD refer to the test fuel, CF diesel, and the undoped methane/air flame.

Viscosity Measurements

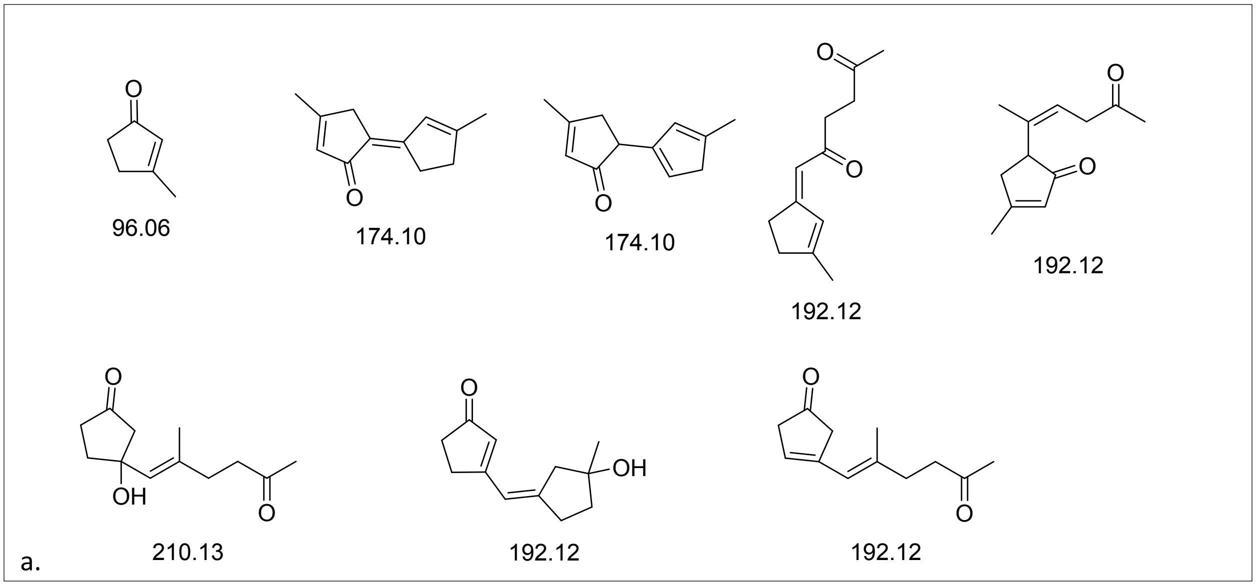
Only the HD-HDO* product was tested for viscosity due to its unusually high viscosity, the other analogs appeared within norm. Sample was analyzed for density and viscosity using an Anton Paar SVM 3000 /G2 Stabinger Viscometer. Approximately 3mL of sample was loaded into the instrument cell for measurement. A preset mode of 'repeat' was chosen to measure with fast precision and a repetition value of 3. The sample was analyzed at 20 °C and 40 °C. Viscometer calibration was checked at 20 °C using a certified N26 viscosity reference standard purchased from Cannon Instrument Company.

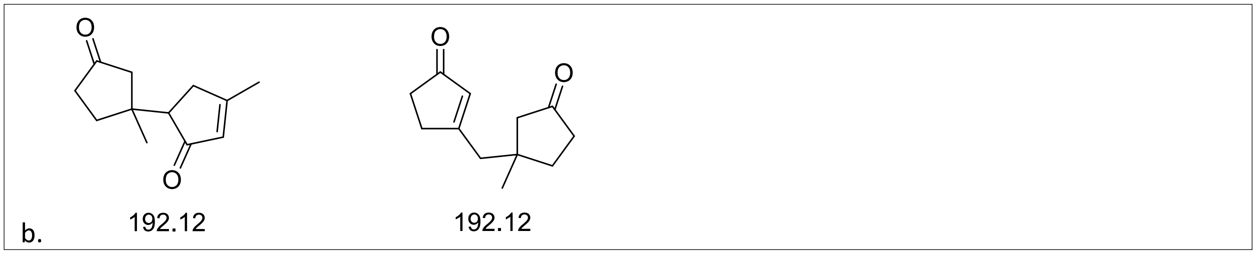
Results and Discussion

We first screened aldol condensation conditions for the three ketones to identify suitable conditions for scale-up, then scale-up was performed and product compositions were analyzed in detail. The products were then hydrotreated and compositional analyses were performed on the resulting mixtures; finally fuel properties of these mixtures were evaluated and discussed.

Aldol Condensation

Our rationale for selecting the three starting materials cyclopentanone, cyclohexanone, and 2,5-hexanedione as explained in the introduction, was threefold: the availability of the starting materials from bioderived sources, the potential for multicyclic products via aldol chemistry, and potential for a scalable synthesis of these analogs. Although HD is not a cyclic system, it readily forms MCP (See Scheme 1), which then becomes the starting material for a cascade of aldol condensations and Michael additions. Cyclopentanone and cyclohexanone form dimers as the main products even under prolonged heating, along with minor (less than 10% as estimated by ^{1}H NMR and GC) amounts of trimers. Unlike the other two starting cyclic compounds, HD formed, aside from MCP, a variety of oligomers and fused ring species in about 50% yield based on 97-99% conversion from HD. Because MCP can theoretically undergo both aldol condensation and Michael addition, there are further opportunities for continued ring formation and the exact structures of reaction products are challenging to determine. Shown in Figure 3a and 3b are the theoretical products of aldol and Michael addition of HD and MCP up to the first C-C bond formation, respectively. One can envision that these species become intermediates for further in situ condensations and additions. NaOH can abstract a proton from multiple MCP sites, adding to the complex product profile. Figure 3c provides examples of MCP resonance structures that can form under basic conditions. Further evidence of oligomerization/cyclization/aromatization is the thickening of the reaction mixture, and in some cases, even formation of solid products (Table 1).





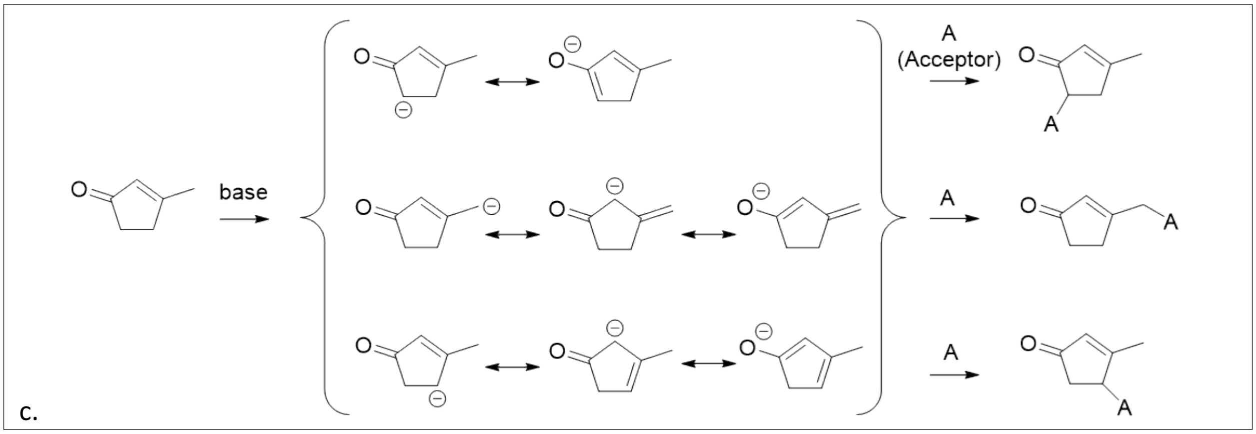


Figure 3. **(a)** Possible aldol condensation products predicted for MCP and HD and their respective exact calculated mass. **(b)** Possible Michael addition products predicted for MCP and HD and their calculated mass. **(c)** MCP resonance structures under basic conditions. The acceptor A is a ketone or α, β-unsaturated carbonyl compound.

It is important to emphasize that while all aldol products are valuable fuel intermediates, we aspired for a mixed product of dimers, trimers and low molecular weight oligomers, to provide a wide boiling range profile of the final hydrotreated product. In addition, the goal of this research was to identify simple, viable routes that were scalable above 100 g with minimal optimization, as relatively large quantities were required for testing. In order to determine the best conditions for each of the starting materials, we screened many catalysts on small scale. Shown in Table 1 are all the conditions performed for each of the starting materials. The screening process typically comprised of small-scale reactions (5 g or less) and only those with high conversions were then scaled up to 100 - 200 g batch sizes.

Table 1. Process parameters to optimize/screen/reactions that use HD, Cp and Ch as starting materials.

Starting materials	**Total mass of starting material (g)**	**Catalyst (g)**	**Journal reference**	**Solvent**[a]	**Time (hrs)**	**Conversion to dimer/oligomer (mol%)**
Cyclohexanone	1.05	[b]	37	Acetonitrile	10	85-95
Cyclohexanone	5	LiOH - 0.116	38	EtOH	72	0
Cyclohexanone	5	K_2CO_3 - 0.667	39	Neat	72	10
Cyclohexanone	5	K_3PO_4 - 1.11	22	Neat	72	72

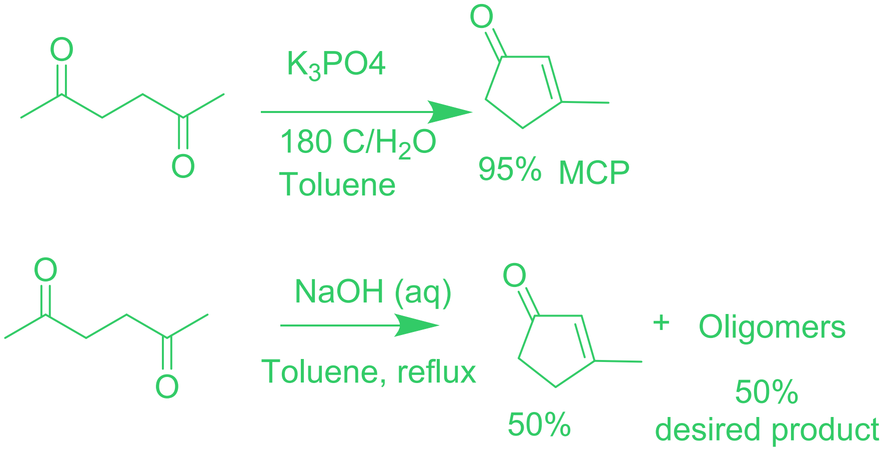
Cyclohexanone	50	NaOH - 3.00	40	H_2O	72	0
Cyclohexanone	25	NH_3HSO_4 - 2.34	41	Neat	72	74
Cyclohexanone	200	NH_3HSO_4 - 19.7	24	Neat	72	75-80
Cyclopentanone	5	$RuCl_3$ - 0.247	42	Neat	24	50
Cyclopentanone	5	TMG - 0.709	43	Neat	36	2
Cyclopentanone	5	NH_3HSO_4 - 0.549	24	Neat	72	25
Cyclopentanone	5	K_3PO_4 - 1.30, PEG300 - 1.00	22	Neat	48	75-80
Cyclopentanone	22	NaOH - 1.01	23	H_2O	48	95
Cyclopentanone	200	NaOH - 2.44	23	H_2O	72	80-90
2,5-Hexanedione	3	K_3PO_4 - 0.704, PEG300 - 0.5	22	Neat	48	Solid product
2,5-Hexanedione (Parr reactor)	24.4	K_3PO_4 - 4.54	22	Toluene, H_2O	1	35
2,5-Hexanedione	5	K_3PO_4 - 1.00	22	Toluene, H_2O	48	50
2,5-Hexanedione	3	NH_3HSO_4 - 0.297	24	Neat	48	Solid product
2,5-Hexanedione	4	NaOH - 0.210	14	H_2O	24	Solid product
2,5-Hexanedione	200	NaOH - 7.00	27	Toluene, H_2O	24	95

[a] All reactions were executed at or near reflux, 100-115 °C. [b] Stoichiometric non-catalytic reaction with equivalent amounts of NaI and TMSCl.

2,5-hexanedione (HD)

Our initial investigations were based on the self-aldol condensation of HD reported by Sacia et al.[14] whose work focused on generating MCP, not oligomers. Cyclizing HD with K_3PO_4, saturated Na_2SO_4, and toluene for 1 hr at 170-180 °C in the Parr reactor produced MCP as the main product with selectivity as high as 97-98%, essentially without any oligomerization (Scheme 1). Conditions were optimized to increase the yield of oligomers with a conversion of about 50%, along with about 10% residual HD and about 40% MCP (estimated from GC). Although this method generated an acceptable fraction of oligomers, the scale was limited by the volume of the Parr reactor (300mL) and the quantity of the starting material HD (20-30g) and further deemed undesirable due to incomplete conversion of HD. The Parr reactor set-up was not feasible for scale-up, considering the limited yield per run. Due to this limitation, trials began on

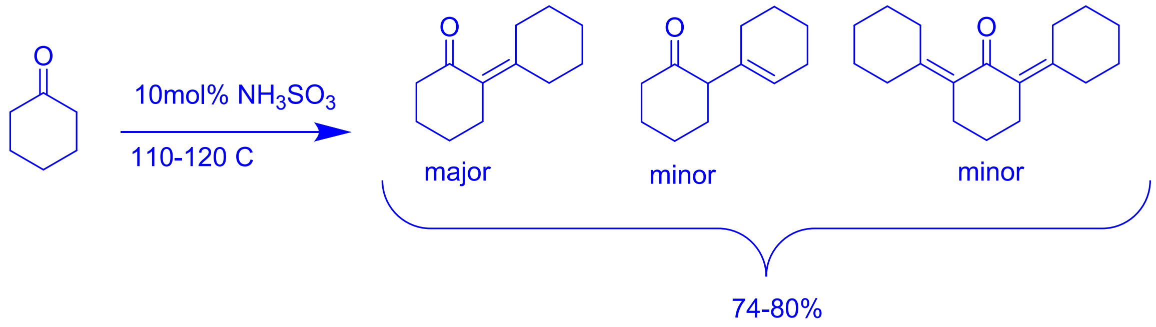
HD oligomerization conditions in typical organic chemistry set-ups (round bottom flask affixed with condenser), with gentle atmospheric reflux over the span of 1-3 days. Many conditions were executed to improve the yield of MCP oligomers, but generally it appeared that the reaction was equilibrium-limited because the conversion to oligomers was roughly about 50% alongside 50% MCP (molar ratios), in the best cases. The use of NaOH (aqueous) as a catalyst in toluene under reflux for 2 days provided the highest conversion of HD coupled with the highest yield of oligomers. The advantage of this approach was that 200g of material could be produced in one batch, in a 500mL round bottom flask affixed with a condenser. MCP and residual solvents were removed by vacuum distillation. The distillation yielded 133.5g of mixed cyclic products which corresponds to a 79% recovery, based on 1.75mol of starting material shown in scheme 1.



Scheme 1. Aldol condensation of 2,5-hexanedione; conversion and product profile were estimated from ^{1}HNMR and GC-MS. The conversion of the second reaction was 100%, based on complete consumption of the HD starting material. The percentages shown are molar ratios.

Cyclohexanone (Ch)

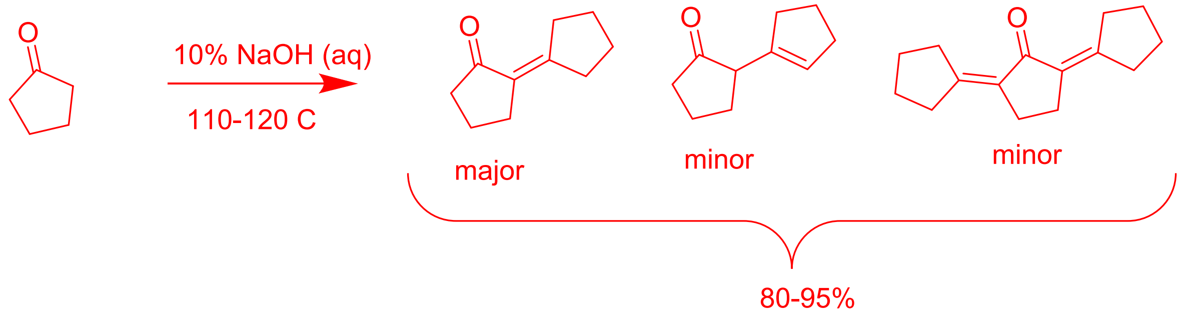
The self-condensation of cyclohexanone was also probed with a variety of acid and base catalysts (conditions in Table 1). Surprisingly, the NaOH/toluene reaction condition, which was effective in the HD aldol condensation, did not result in any product formation when used with cyclohexanone. Many of the bases did not provide a high conversion of cyclohexanone to the dimer product 2-cyclohexylidenecyclohexanone, with the exception of K_3PO_4 in presence of PEG300. When run for 24 hours, the reaction with K_3PO_4 and PEG300 gave a low conversion of 50%. Upon longer heating (2 days) the same conditions resulted in a 72% conversion from the starting material. In parallel, we were screening conversion rates with sulfamic acid (NH_3SO_3) as a catalyst, which provided a conversion efficiency of 74%, similar to the K_3PO_4/PEG300 system. The use of the sulfamic acid catalyst was deemed superior over the K_3PO_4/PEG300 combination due to PEG300 causing contamination issues. During the work up of the K_3PO_4/PEG300 reaction, not all PEG300 partitioned into the aqueous layer and remained as a contaminant in the organic layer unable to be removed by subsequent distillation due to its high boiling point (>200 °C). A scale up with cyclohexanone and sulfamic acid gave 74-80% conversion based on starting material consumption, leading to the dimer as the major product, and small amounts of trimers and other byproducts (Scheme 2). The aldol mixture was vacuum distilled to remove starting material and yielded 117.5g of product out of 163g possible based on 3.03mol of starting material (72%).



Scheme 2. Self-aldol condensation of cyclohexanone and its products. The conversions were estimated from ^{1}HNMR, and product profile from GC-MS. The 74-80% is the conversion to products, based on the consumption of cyclohexanone starting material.

Cyclopentanone (Cp)

Various reported conditions of similar reaction systems were tested for the aldol of cyclopentanone. Hydrated $RuCl_3$ catalyst only offered a conversion of 50% and a laborious work-up to purify the product. Surprisingly, yields were low when using the sulfamic acid catalyst which worked well for the cyclohexanone counterpart, resulting in conversion ranging from 2-50% of the main dimer product. K_3PO_4 and PEG300 showed a similar conversion to the cyclohexanone, around 75%, however this method suffered from the same PEG contamination issues mentioned earlier. Aiming for a higher yield and cleaner product, the aldol was performed with 10% aqueous NaOH (0.01 equivalents with respects to cyclopentanone) at reflux for 2 days, which led to 95% conversion at small scale. The reaction proved scalable, as a high conversion was also demonstrated for 100-200g scales, with conversion varying from 80 to 95% of the main dimer product, 2-cyclopentylidenecyclopentanone. Scheme 3 shows the products of the cyclopentanone/NaOH reaction. The aldol condensation products were purified only via removal of starting material by vacuum distillation, with a recovery of 124.3g (82%, based on 2.29mol of starting material).



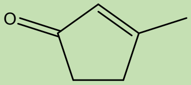
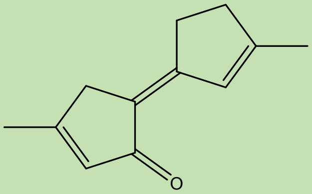
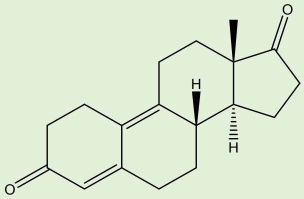
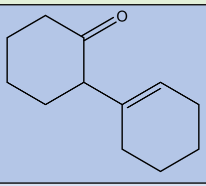
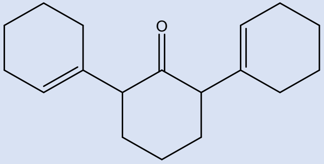
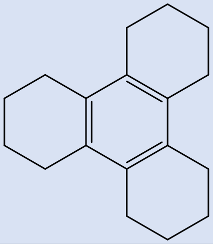
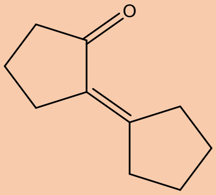
Scheme 3. Self-aldol condensation of cyclopentanone reaction and its reaction products. The conversion and product profile were estimated via ^{1}HNMR and GC-MS. The 80-95% is the conversion to products, based on the consumption of cyclopentanone starting material.

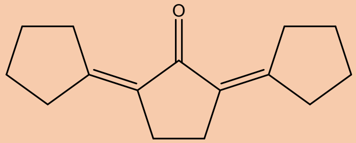
Given that both cyclopentanone and cyclohexanone failed to yield significant amounts of oligomers, we attempted to subject mixtures of MCP and cyclopentanone to aldol reaction conditions. One such example included combining MCP with cyclopentanone, with NaOH as the catalyst in toluene, since these two starting materials had high conversions under similar reaction conditions. This experiment resulted in minimal product conversion (around 43%) and products were difficult to decipher via ^{1}HNMR due to major overlap of the starting materials and products, and the approach was abandoned.

GC Analysis of Aldol Mixtures

The aldol condensation products were analyzed via GC-FID and GC-MS to evaluate the product profile and confirm the identity of the products. The HD aldol product was very viscous and had to be dissolved in THF to be analyzed. GC indicated the presence of residual MCP which could not be distilled off without causing further oligomerization/polymerization during heating, and formation of fused-ring species. Major species identified in the GC-MS are found in Table 2 (entries 1-3) along with unidentified complex molecules that appear in relatively high abundance. The dimer of MCP aldol, 3',4-dimethyl-[1,1'-bi(cyclopentylidene)]-2',3-dien-2-one, was detected in the GC-MS, but it was a minor product. The aldol product of HD and MCP (m/z 192g/mol) was not detected via GC-MS. Although it is clear that HD undergoes complex chemistry evident by GC-FID/MS, it is difficult to identify main components other than those mentioned. It is also important to note that multicyclic fused ring compounds are likely not volatile enough to make it through the GC column (260-325 °C). In order to probe for the presence of oligomers, GPC-SEC of the HD-derived product was conducted (GPC traces can be found in the Supplemental Information – Figure S4). The M_n and M_w of the detected species were 670g/mol and 918g/mol, respectively. These molecular weights may be due to oligomers, but more likely to fused ring complex structures.

Table 2: Species present in the HD-, Ch- and Cp- aldol products after distillation.

Entry	**Starting material***	**Compound name**	**m/z (g/mol)**	**Area**	**Structure**
1	HD-derived	3-methyl-2-Cyclopenten-1-one	96.05	4.44x10^{8}	
2	HD-derived	3',4-dimethyl-[1,1'-bi(cyclopentylidene)]-2',3-dien-2-one	174.10	2.91x10^{8}	
3	HD-derived	19-norandrosta-4,9-diene-3,17-dione	270.16	1.18x10^{8}	
4	HD-derived	Unknown	348.28	3.32x10^{8}	Unknown
5	HD-derived	Unknown	228.07	6.77x10^{8}	Unknown
6	Ch-derived	2-(1- cyclohexenyl) cyclohexanone	178.13	2.78x10^{9}	
7	Ch-derived	[1,1':3',1''-tercyclohexane]-1,1''-dien-2'-one	258.14	6.44x10^{8}	
8	Ch-derived	1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-triphenylene	240.18	1.74x10^{8}	
9	Cp-derived	2-cyclopentylidenecyclopentanone	150.10	1.71x10^{10}	

10	Cp-derived	2,5-dicyclopentylidene cyclopentanone	216.15	8.69×10^8	

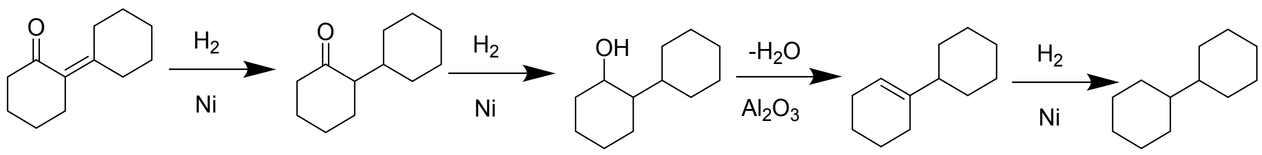
*Darker shades indicate the major species while lighter shades indicate the minor species.

Cyclohexanone (Ch) aldol proceeded and as predicted, the main product was the dimer 2-(1-cyclohexenyl) cyclohexanone (Table 2, entry 6) with minor products shown in Table 2, entries 7-8. The GC-FID traces from the Ch-aldol product and Ch-HDO product were overlapped (Figure 4b) and it appears that the areas % of the HDO product is larger than area % of the aldol product. One explanation is that other multicyclic species had formed during the Aldol condensation, which are not visible via GC, but the hydrotreatment protocol resulted in the chemical or thermal breakdown of those compounds into the desired bicylohexane product.

Cyclopentanone (Cp) also behaved as expected under aldol condensation conditions, forming mainly the dimer and small amount of trimer, as shown in Table 2, entries 9-10.

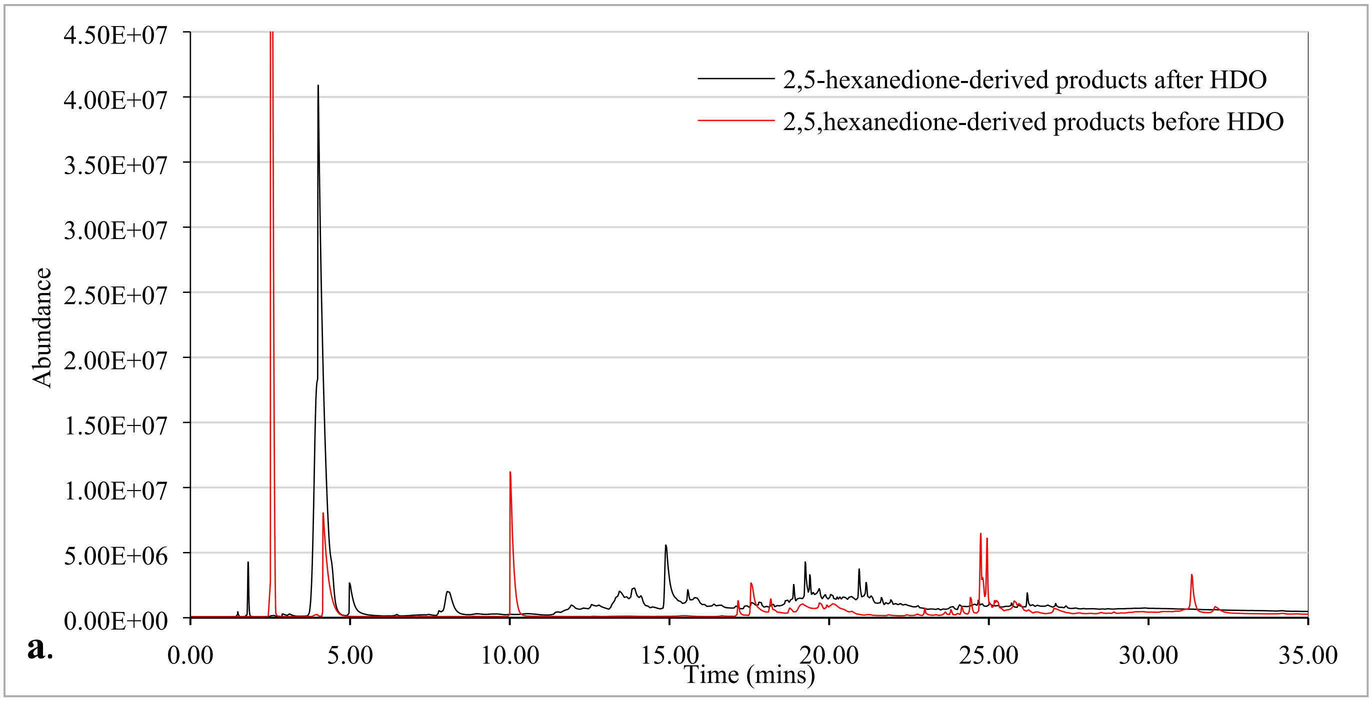
Hydrodeoxygenation-Hydrogenation (HYD-HDO)

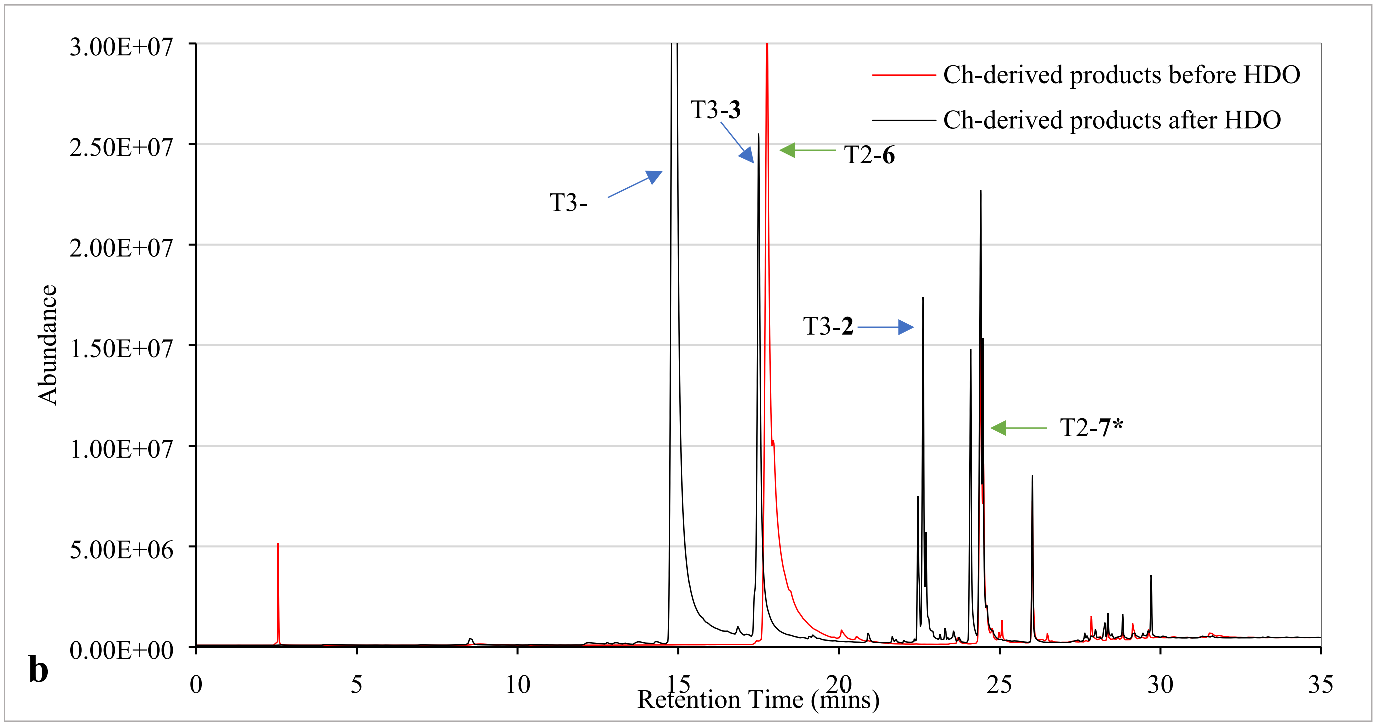
Hydrotreatment (-HDO) of the mixture of dimers and oligomers generated from aldol condensation of ketones was conducted to remove the carbonyl (C=O) and the olefinic functional group (C=C) to produce polycyclic hydrocarbons that can meet diesel specifications. Initial hydrotreating experiments on oligomer mixtures from HD were conducted over a Pd catalyst on carbon support (Pd/C) at varying temperatures between 150 and 200 °C and operating pressure above 1000 psig. The ^{13}C NMR analysis of the resulting product showed significant reduction of both the carbonyl and the olefinic functionalities, however, the formed alcohol remained unaffected. Literature reports indicate that bi-metallic catalysts such as Pd-Ru and Pd-Re can successfully hydrodeoxygenate vanillyl alcohol and lignin.[44] Therefore, we also explored Pd-Re catalyst supported on carbon at 200 °C and 1000 psig. The addition of Re improved the C=C hydrogenation but the HDO of C=O was incomplete, still generating a significant amount of alcohol alongside the desired hydrocarbon. The mentioned protocols were also applied to cyclohexanone and cyclopentanone-derived products, with similar results (i.e. large amounts of hydroxy containing species remaining). We concluded that an acidic catalyst was needed to efficiently complete the dehydration step and remove the oxygen. Ni supported on alumina (Ni-Al_2O_3), which is a commercially available catalyst, was used at 250 °C and 800 psig in the hydrotreatment of the mixture derived from the aldol condensation of cyclohexanone-. The ^{13}C NMR analysis of the products confirmed a near complete conversion to cyclic alkanes, (NMR spectra can be found in the Supporting Information, Figure S2b, S2d, and S9b). The same protocol was applied to the oligomeric mixtures derived from HD and Cp. The HD mixture was very viscous after the removal of MCP by distillation, so it had to be dissolved in a solvent that could be easily converted into a light fraction during hydrotreatment and not interfere with the catalyst. We selected tetrahydrofuran, which could dilute the feed to facilitate its pumping into the reactor, and then be removed by transforming into highly volatile byproducts (butanes) under hydrotreating conditions. Trace amounts of THF can still be found in the hydrotreated product, but because we strived to mimic a large scale-methodology, it was left in, without further processing, unless noted otherwise. The HDO reaction is illustrated for cyclohexanone aldol condensation in Scheme 4.



Scheme 4. Illustrative example of hydrogenation-deoxygenation of the product of aldol condensation of cyclohexanone.

The hydrodeoxygenated samples were analyzed by GC-FID and NMR to determine the conversion and identify products. The GC-FID overlays of hydrodeoxygenated products from HD, Ch and Cp, respectively are shown in Figure 4.





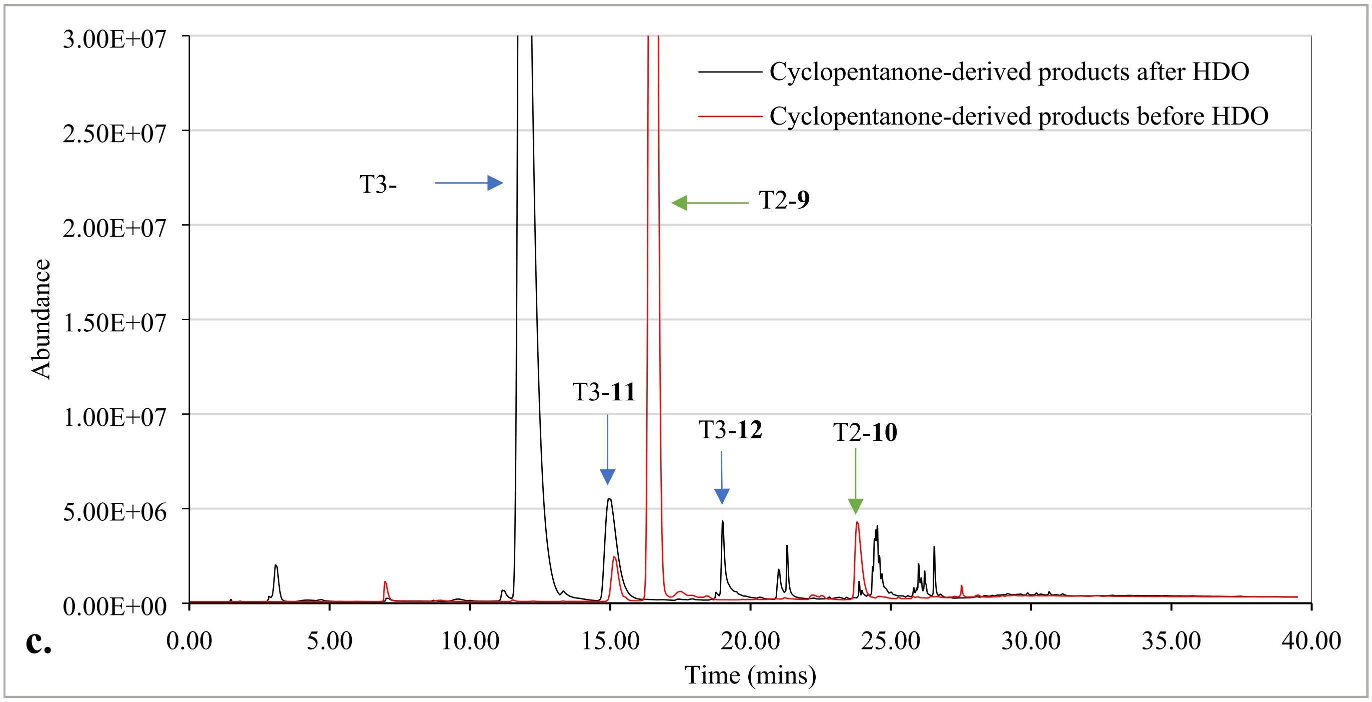


Figure 4. The GC-FID overlays before (red) and after (black) hydrotreatment: **(a)** 2,5-hexanedione – HD, **(b)** cyclohexanone-Ch, **(c)** cyclopentanone – Cp. Retention time can be found on the x-axis (min) and the abundance response can be found on the y-axis. The arrows

correspond with either Table 2 (T2) or Table 3 (T3) and their respective sample entry number. *T2-**7** is overlapped with another compound ~ 24.5 mins.

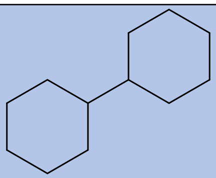
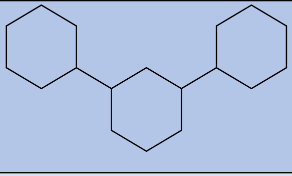
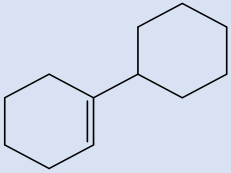
The hydrotreated product of cyclohexanone coupling (Figure 4b) has a relatively simple product profile consistent with the formation of the main dimer product and trimer product (Table 3, entries 1-2) together with other minor products of partial hydrodeoxygenation or complex addition (Table 3, entries 3-7). The GC-MS of all aldol condensation products, HDO products, and their overlay spectra, can be found in the supporting information. Interestingly, Figure 4b displays a higher concentration of HDO product (black trace) versus aldol precursor (red trace), which would suggest that higher molecular weight, potentially multicyclic species are present in the sample, but are not detectable via GC (non-volatile). The large bicyclohexane desired peak appears to be a breakdown product of those species during hydrotreatment, which would be consistent with such difference in the magnitude of the peaks.

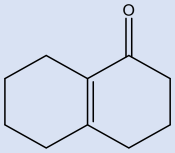
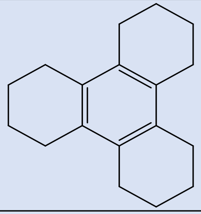
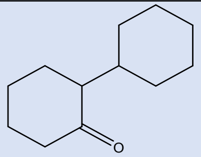
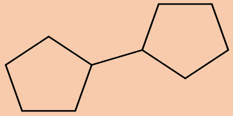
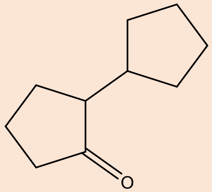
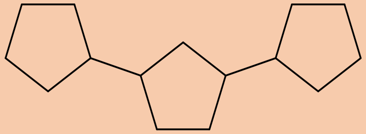
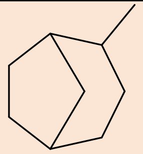
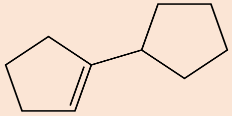
Similarly, the GC-FID of the hydrodeoxygenated product of the cyclopentanone condensation (Figure 4c) displays a simple product profile consistent with the formation of the main dimer product (Table 3, entry 10), the trimer product, (Table 3, entry 12), along with other partially hydrotreated products, or other structures resulting from complex chemistry (Table 3, entries 11, 13-18).

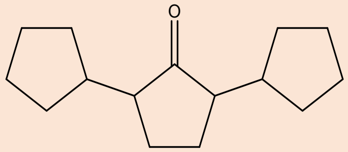
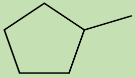
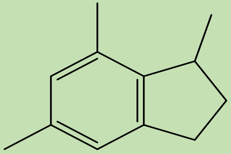
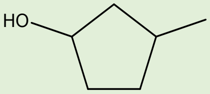
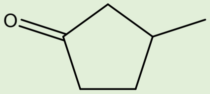
The HD-derived hydrodeoxygenated product (Figure 4a) once again proved challenging to decipher. The GC-FID and GC-MS indicated that the major species present are a result of MCP hydrotreatment, although ^{1}HNMR shows a complex mixture of other products. This is likely due to the presence of multiple multicyclic ring structures which did not volatilized during GC analysis. GPC confirmed the presence of species with M_n and M_w of 602 and 849 g/mol, respectively which might make up a large portion of the sample. Although there was residual

MCP in the aldol product, methylcyclopentane appears to be the dominant product in the HDO mixture, which further supports the hypothesis that most of the sample was not GC-able. Further evidence is provided by ^{1}H NMR (Figure S2a in the Supplemental Information) which shows the absence of MCP and presence of a small amount of its hydrogenated product. The bulk of the sample is a mixture of complex products whose peaks overlap between 1-3ppm. The ^{13}C NMR shows a large amount of alcohol, although hydroxy is not detected in the proton spectrum (the anomaly is common). Overall, the spectroscopic data shows a less efficient transformation of 2,5-hexanedione into an MCP dimer versus the other two starting materials. Subsequent to the hydrodeoxygenation process, the small amount of residual ketones (<2%) is not expected to affect the swelling of elastomers as they are known to do,[45] but further work may be required to demonstrate. This may become significant during storage, transport and use of these fuels, where seals made up of elastomers are present.

Table 3: Species found via GC-MS in the Ch-HDO, Cp-HDO and HD-HDO products.

Entry	**Starting material**	**Compound name**	**m/z (g/mol)**	**Area**	**Structure**
1	Ch-derived	1,1'-bicyclohexyl	166.17	7.33x10^{9}	
2	Ch-derived	1,3-tercyclohexyl	248.25	1.16 x10^{9}	
3	Ch-derived	1-cyclohexyl-cyclohexene	164.15	2.55x10^{9}	

4	Ch-derived	3,4,5,6,7,8-hexahydro-1(2H)-naphthalenone	150.10	1.7 x10^9	
5	Ch-derived	Unknown	150.05	8.99x10^8	Unknown
6	Ch-derived	1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-triphenylene	240.18	4.37x10^8	
7	Ch-derived	[1,1'-bicyclohexyl]-2-one	180.15	3.29x10^8	
10	Cp-derived	1,1'-bicyclopentyl	138.14	9.87x10^9	
11	Cp-derived	[1,1'-bicyclopentyl]-2-one	152.12	1.74x10^9	
12	Cp-derived	1,3-dicyclopentylcyclopentane	206.20	3.63x10^8	
13	Cp-derived	Unknown	194.02	4.36x10^8	Unknown
14	Cp-derived	2-Methylbicyclo[3.2.1] octane	124.12	2.76x10^8	
15	Cp-derived	Unknown	198.07	2.74x10^8	Unknown
16	Cp-derived	1-cyclopentylcyclopentene	136.12	1.14x10^8	

18	Cp-derived	1,5-Bis(cyclopentyl)-1-cyclopentanone	220.18	1.43x10^8	
13	HD-derived	methylcyclopentane	84.09	1.43 x10^9	
14	HD-derived	2,3-dihydro-1,5,7-trimethyl-1H-Indene	160.12	1.12x10^9	
15	HD-derived	3-methyl- cyclopentanol	100.08	1.09x10^8	
16	HD-derived	3-methyl-cyclopentanone	98.07	1.52 x10^8	

Darker shades indicate the major species while lighter shades indicate the minor species.

Elemental analysis of each aldol product versus hydrotreated product shows in each case an increase in % C and % H and decrease in % O, as expected. The % O was determined by deviation from 100%, assuming no other elements were present in the sample. Notably, the reduction of oxygen in the HD-HDO product is likely due to drying and subsequent loss of THF, butanol (byproduct of THF hydrotreatment) and potentially other volatile species present in the mixture originating from MCP, and not hydrotreating efficiency. As corroborated by GC-MS and NMR, there is a small amount of oxygenates still present in all samples.

Table 4. Elemental analysis of aldol and HDO products

MIXTURE	% C	% H	% O
HD-ALDOL	78.6	8.78	12.7
HD-HDO	83.8	11.8	4.38
HD-HDO*	87.5	12.1	.130
CH-ALDOL	80.2	10.1	9.71

CH-HDO	84.9	13.1	2.02
CP-ALDOL	79.1	9.60	11.3
CP-HDO	85.3	12.9	1.61

Fuel properties of the three mixtures were evaluated which include simulated distillation, lower heating values (LHV), derived cetane numbers (DCN), density, an alternative method to determine yield sooting index of mixtures, cold flow properties and flash point to evaluate suitability of the HYD-HDO materials as diesel blendstocks and compliance with ASTM D975 - 20a standard specification for diesel fuel.[46]

Simulated Distillation

Simulated distillation was conducted on the Ch, Cp and HD and HD* (dried) mixtures after hydrotreatment via ASTM D2887, and the T10, T50 and T90 values are reported in Table 5. The ASTM D975 require that T90 as determined via simulated distillation for a No. 2-D fuel have a minimum of 300 °C and a maximum of 356 °C. For a No.1-D, the maximum T90 is not specified, only a minimum of 304 °C. Given these guidelines, it appears that the Cp product does not meet either of the requirements, due to its low T90, while the HD-HDO* T90 is too high. While HD-HDO* is too viscous the Cp product is still perfectly suitable as a component in a finished fuel that falls under the proper boiling range. The low T10 of HD-HDO is expected due to residual THF co-solvent that was used for hydrotreating, butane and butanol that are present in the final mixture. THF was a necessary co-solvent since some of the by-products solidified during the distillation process, rendering the final mixture exceedingly viscous. Considering that these mixtures had intentionally minimal processing (i.e. no final distillation), contain a range of boiling fractions and have not been optimized in any way, these results are very encouraging.

Table 5. Predicted ASTM D86 parameters of the distillation curves for the three mixtures, derived from the simulated distillation data.

COMPOUND	CH-HDO	CP-HDO	HD-HDO	HD-HDO*	DIESEL QC
T10 (°C)	248.8	204.8	87.8	233.8	202.4
T50 (°C)	238.8	191.4	229.9	320.0	260.8
T90 (°C)	332.7	247.3	421.9	494.8	325.3

Ch-HDO, Cp-HDO, HD-HDO denote the hydrodeoxygenated samples obtained from the aldol condensation of Ch, Cp and HD respectively. HD-HDO* originates from a sample which was dried to remove butane and THF but potentially removed other volatile fractions. All samples were run in accordance with ASTM D 2887.

Figure 5 shows the complete distillation curves for the three mixtures discussed in Table 5 and compared to a standard diesel #2 quality control sample. It is evident from the graph than the Ch- and Cp-derived samples have a similar distillation profile and range to the standard, while the HD sample has a much lower T10, and a high T90, and HD* sample has very high both T10 and T90, due to high content of fused cyclic mixtures, that are likely solid and increase the boiling point of the overall mixture. Due to the dimer being the major component in both Ch-HDO and Cp-HDO mixtures, both curves have a flat region, which in neat form, makes them less attractive as diesel fuels. These mixtures are however suitable as blending components into a diesel fuel for optimal operability over a broad temperature range. The distillation curve suggests the need for a broad boiling range mixture, when a diesel is formulated, further confirming our approach in not distilling final products or aiming for a single component.

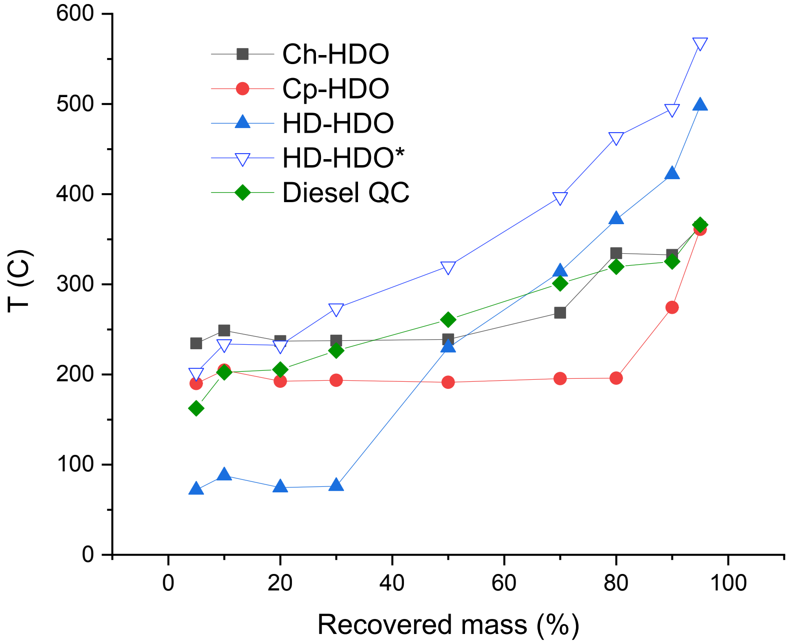


Figure 5. Predicted ASTM D86 distillation curves for the HDO products of the reactions of Ch, Cp and HD oligomerization. The predicted curves were obtained from the Simulated Distillation data collected according to the ASTM D 2778 method. Diesel QC is a #2 diesel fuel. The HD-HDO curve originates from HD-HDO as obtained from hydrotreatment, while HD-HDO* originates from material that was dried to remove butane, THF and unintentionally other light fractions.

Lower Heating value (LHV)

The lower heating value (LHV) or higher heating value (HHV) of a fuel or fuel component is an important consideration when selecting or formulating a fuel. When a hydrocarbon fuel is burned one product of combustion is water. The quantity of water (steam) produced stores a small fraction of the energy released during combustion as the latent heat of vaporization. Although the measurable parameter is the higher heating value (HHV), the LHV is typically reported because it gives a net caloric value to the fuel. LHV is derived from HHV and it depends on the hydrogen content of the mixture shown in Table 4. Table 6 summarizes LHV values, densities, cetane numbers and normalized sooting concentrations.

Table 6. LHV values, density, cetane number and normalized soot concentration for each of the final hydrotreated mixtures, Ch, HD and Cp.

SAMPLE	LHV (MJ/KG) AVERAGE OF THREE RUNS	LHV STD. DEVIATION	DENSITY (G/CM^3)	DCN	IGNITION DELAY (MS)	NSC*
CH-HDO	40.70	0.09	0.872	40.9	5.1	0.494
HD-HDO	37.39	0.34	0.847	24.5	9.77	0.759
HD-HDO*	39.91	0.07	-	-	-	-
CP-HDO	41.54	0.35	0.860	42.6	4.89	0.577

*NSC values are determined relative to CF diesel, a certification diesel fuel.

The LHV values of both Ch-HDO and Cp-HDO mixtures are quite high and in line with expected cyclic hydrocarbons, despite their residual oxygenates content from HDO, further demonstrating the validity of the approach. The LHV and density values are only slightly lower than those reported.[47] Pure Ch-HDO was reported to have an LHV of 42.97 MJ/Kg, while pure Cp-HDO had an LHV of 42.42 MJ/Kg. While these values are slightly higher (by 5% and 2% respectively) than our experimental values, they may not justify extra steps and cost incurred during purification/distillation, since the crude Cp and Ch products still have commendable LHVs. The HD mixture has a relatively high content of alcohol (confirmed by the ^{13}C NMR), and thus a lower percent hydrogen and lower LHV, but the LHV remains still within acceptable levels. The removal of THF and butanol in the HD-HDO* dried sample reduced the amount of oxygenate in the sample which boosted the LHV near 40 MJ/Kg. However, the viscosity increased substantially: at 20 °C – 485 cSt, viscosity at 40 °C – 95.7 cSt.

Flash Point and Cold Flow Properties

The cold flow properties of all analogs are acceptable for diesel fuel blendstocks, as illustrated in Table 7. Notably, the dried HD-HDO* sample was remeasured, with no consequences in the freeze point, but substantial improvement in the flash point. As expected, with volatiles such as THF, butane, butanol removed, the flash point increased dramatically, and is within an acceptable range.

Table 7: Freeze, cloud, pour and flash point properties of final mixtures against a diesel standard

Sample[b]	Freeze point (°C)	Cloud point (°C)	Pour point (°C)	Flash Point (°C)
Ch-HDO	-6.8	-34.3	-36.0	88
HD-HDO	-56.1	-67.4	< -36.0[a]	31
HD-HDO*	-56.0	-86.3	0.0	83
Cp-HDO	-38.3	-60.1	-57.0	53
Diesel QC	-43.1	-11.7	-19.3	68

[a] Sample HD-HDO was smaller than the amount required for pour point testing. The insufficient sample amount could lead to a low optical signal, which is likely the reason for “below -36.0 C” showing as the final result.[b] All samples were run in accordance to ASTM method D975.

Derived Cetane Number (DCN)

Measurements were conducted at Southwest Research Institute per ASTM D6890 – ignition delay and derived cetane number of diesel fuels by combustion in a constant volume chamber. The results are shown in Table 6. The samples measured are the final *as-obtained* samples from hydrotreatment, without further processing.

The DCN of both cyclohexanone and cyclopentanone derived products exceed 40, which is a requirement for diesel fuel in the US. The HD-derived product has a lower DCN, not entirely unexpected due to its higher oxygen content, including THF and butanol. Had the product been dried to remove these hydrotreatment residual components, it would have become too viscous to measure DCN. Further optimization of synthetic and hydrotreating processes will likely enable improvement of the cetane numbers for these blendstocks.

Sooting Tendency

Table 6 lists the measured NSCs for the fuels. In all cases the value is less than 1, indicating that these fuels produced less soot when doped into a methane/air flame than the CF certification diesel fuel. The NSC of the HD-HDO product (0.759) versus the Ch and Cp-HDO products (0.494 and 0.577, respectively) show that both the Ch and Cp-derived products have a lower sooting tendency compared to HD-dervied products, but overall the results suggest that these bio-derived fuels have low sooting tendencies and would reduce particulate emissions from compression-ignition engines compared to a real diesel.

Conclusions

Reports of processes which are scalable, employ simple, inexpensive, readily available off-the-shelf catalysts, and yield acceptable fuel property products, are inexistent in the published literature. The processes described herein can be adopted by industry precisely because they involve minimal purifications and provide final mixtures in high yields. Our work shows the utility of cyclic ketones (cyclopentanone and cyclohexanone) and 2,5-hexanedione as starting materials with well-established routes from biomass, for the selective production of condensates via Aldol chemistry and Michael addition. Subsequent hydrotreatment provides mixtures that meet many specifications for diesel fuel. Of the three starting materials, the cyclopentanone and cyclohexanone-derived products were more promising than the 2,5-hexanedione-derived products since the latter had a relatively high content of heavy fractions, likely multicyclic structures. After extensive catalyst screening that enabled to prepare aldol products in high yield, we identified suitable and mild conditions to accomplish the aldol condensation, which were carried out at 200g scale. Specifically, we found that for cyclohexanone (Ch), sulfamic acid provided the best conversion of 75-8-%, cyclopentanone (Cp) worked best with 10% NaOH (aq) catalyst, neat to provide 80-90% yield of product, while 2,5-hexanedione (HD) yielded a mixture of MCP and oligomers/fused ring species above 95% yield, based on near quantitative conversion of HD. It is important to emphasize that while all aldol products are valuable fuel intermediates, we targeted a mixed product of dimers, trimers and light oligomers, to provide a wide boiling range profile of the final hydrotreated product, beneficial for diesel. The product profile was evaluated via GC-FID, GC-MS and NMR after every step. While Ch and Cp provided rather clean mixtures mostly containing target compounds, the HD-derived mixture proved complex, but overall indicating the preferential chemistry towards Michael addition of MCP than aldol condensation; MCP was the only aldol condensation product detected (50%), with subsequent chemistry consistent with Michael addition of MCP (50%). The aldol mixtures were subjected to hydrodeoxygenation in presence of an acid catalyst, Al_2O_3 which efficiently resulted in mainly bi-Cp and bi-Ch and small amounts of respective trimers. In contrast, the HD-aldol mixture, under the same conditions, produced an equally complex mixture that, based on HNMR and GC data, we ascertained it was made-up mostly of heavy multicyclic species (M_w 642 g/mol) resulting in a very viscous mixture.. The fuel properties of the hydrodeoxygenation products were evaluated. The lower heating value were excellent for Ch-HDO and Cp-HDO slightly above 40 and 41MJ/kg, respectively, while slightly lower for processed HD-HDO, near 40 MJ/kg. Follow-on work would examine other catalysts to improve conditions towards complete hydrotreatment and removal of all oxygenates. Similarly, the derived cetane numbers for Ch and Cp are above 40 according to the ASTM D6890 method. The HD hydrotreated product had a much lower DCN of 24, due to oxygenates resulting primarily from the co-solvent (THF) used in the process (residual THF, butanol). The yield sooting index of each mixture was significantly lower than that of a typical diesel (in this case the reference CFA), with the cyclopentanone and cyclohexanone-derived fuel outperforming the 2,5-hexanedione counterpart.

In closing, we have shown a scalable synthesis and efficient methodology to produce cyclic hydrocarbons with encouraging fuel properties that make them potential diesel blendstocks. Furthermore, we have shown that the final products Cp and Ch are tolerant of small amounts of residual oxygenates from nearly complete hydrotreatment, while maintaining desired fuel properties. The presented process is mild, efficient and requires minimal purifications, consistent with cost-efficient methodologies that could be adopted by industry and competitive with current petroleum-based operations.

Author contributions statement

L.C. proposed the synthesis, interpreted data and coordinated collaboration. K.C. conducted experiments, prepared samples, ran NMRs and, and contributed to data analysis. M.S. conducted GC-FID, GC-MS and elemental analysis of samples. S.S conducted hydrotreatment of all aldol samples while K.R. supervised and guided experiments. N. H., C.M. and A.S. conducted and supervised LHV, flash point and cold flow properties experiments. J.Z. performed sooting tendency experiments under C.M. and L.P. supervision who designed those experiments. All authors contributed to and reviewed this manuscript.

Conflict of Interest Disclosure: The authors declare no competing financial interest.

Data Availability: Synthetic procedures, ^{1}H NMR and ^{13}C NMR spectra for samples of interest and all GC-FID, GC-MS chromatograms are available to download from the SI, free of charge.

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