Novel pathways for fuels and lubricants from biomass optimized using life-cycle greenhouse gas assessment

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Correction

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The authors note that Table 1 appeared incorrectly. The corrected table appears below.

Table 1. Self-condensation of ketones in the presence of solid acid/base catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>C&lt;sub&gt;n&lt;/sub&gt;</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Catalyst&lt;sup&gt;†&lt;/sup&gt;</th>
<th>T, °C</th>
<th>Time, h</th>
<th>Conv. 1, %</th>
<th>2 (C&lt;sub&gt;2n&lt;/sub&gt;)</th>
<th>3 (C&lt;sub&gt;3n&lt;/sub&gt;)</th>
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</table>

Ketone (1, 2 mmol), catalyst (200 mg) and toluene (3 mL) was heated in a sealed Q-tube reactor. Conv.1, conversion of compound 1.

<sup>†</sup>Mixture of positional and stereoisomers.
<sup>†</sup>Catalyst MgAlO represents calcined Mg/Al-hydrotalcite (Mg/Al = 3:1) and Nb<sub>2</sub>O<sub>5</sub> represents calcined niobic acid.
<sup>†</sup>Cyclohexane (3 mL) was used as solvent.
Novel pathways for fuels and lubricants from biomass optimized using life-cycle greenhouse gas assessment

Madhesan Balakrishnan*, Eric R. Sacia,a,b, Sanil Sreekumar,a Gorkem Gunbas,c Amit A. Gokhale,a,d Corinne D. Scown,a,e,1 F. Dean Toste,c,f and Alexis T. Bellb,a

*Energy Biosciences Institute, Berkeley, CA 94720; †Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720; ‡Department of Chemistry, University of California, Berkeley, CA 94720; §BP North America, Inc., Berkeley, CA 94720; and ‡Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Decarbonizing the transportation sector is critical to achieving global climate change mitigation. Although biofuels will play an important role in conventional gasoline and diesel applications, bioderived solutions are particularly important in jet fuels and lubricants, for which no other viable renewable alternatives exist. Producing compounds for jet fuel and lubricant base oil applications often requires upgrading fermentation products, such as alcohols and ketones, to reach the appropriate molecular-weight range. Ketones possess both electrophilic and nucleophilic functionality, which allows them to be used as building blocks similar to alkenes and aromatics in a petroleum refining complex. Here, we develop a method for selectively upgrading biomass-derived alkyl methyl ketones with >95% yields into trimer condensates, which can then be hydrodeoxygenated in near-quantitative yields to give a new class of cycloalkane compounds. The basic chemistry developed here can be tailored for aviation fuels as well as lubricants by changing the production strategy. We also demonstrate that a sugarcane biorefinery could use natural synergies between those of conventional biofuels such as sugarcane ethanol. Biofuels | lubricants | life cycle assessment | methyl ketones | greenhouse gases

Countries around the world are enacting legislation to curb greenhouse gas (GHG) emissions. Strategies for decarbonizing road transportation include an array of options from improving engine efficiency and blending bioethanol/biodiesel with gasoline/diesel to using plug-in electric vehicles (1–3). Aviation fuels pose a unique problem because stringent specifications require oxygen-free compounds, limiting the options available (4). Biofuel solutions such as farnesane have been proposed; however, these offer only modest GHG reduction benefits (SI Appendix) and the wide boiling range requirement for jet fuels sets a limit on the amount of single-component renewable fuels that may be blended. At the other end of the spectrum are automotive lubricant base oils where a narrow range of compounds is highly desirable. Poly-α-olefins (PAOs) containing 30 carbon atoms obtained from oligomerization of fossil-derived 1-decene are considered as the benchmark of superior performance for crankcase oils and have a high demand (5). Importantly, the GHG footprint associated with PAO base oils can be higher on a per-mass basis than petroleum-derived fuels if even a fraction of the lubricant is repurposed as fuel at its end of life (6).

The goal of our work was to develop a strategy for the flexible production of jet fuels and lubricant base oils in a Brazilian sugarcane refinery designed to achieve a meaningful reduction in life-cycle GHG emissions. Our approach involves conversion of sugars in sugarcane-derived sucrose and hemicellulose to ketones using a combination of chemical and biocatalytic processes. For example, 2-butanone, can be obtained by the dehydration of fermentation-derived 2,3-butanediol (7, 8) or via chemical/biochemical (9, 10) decarboxylation of levulinic acid (11). The fermentation of various biomass-derived sugars using Clostridia strains produces a mixture of acetone, butanol, and ethanol (ABE), which can be used to synthesize a mixture of monoalkylated/dialkylated ketones (12), specifically 2-pentanone and 2-heptanone. Additional synthons may be produced from bioalcohol-derived olefins (13) or biomass-derived furanic platform molecules, such as 2,5-dimethylfuran and 2-methylfuran, via hydrogenolysis to produce 2-hexanone and 2-pentanone, respectively, with as high as 98% selectivity (14). The biomass-derived methyl ketones are then catalytically self- and cross-condensed to produce C12–C45 condensates, which serve as potential jet fuels (C12–C21) and synthetic lubricants (C33+) after hydrodeoxygenation. We show that our strategy gives a new class of compounds that can be incorporated into production schemes that result in up to 81% reductions in GHG emissions, exceeding even those of conventional biofuels such as sugarcane ethanol.

Results and Discussion

We begin by identifying heterogeneous catalysts and appropriate reaction conditions for the self-condensation of ketones (1) to produce dimer/trimer condensates 2–4 in high overall yield (Table 1). Table 1 entries 1–6 demonstrate that whereas ketones containing methyl functionality at one end undergo selective trimerization to produce isomers of 3 and 4 in the presence of base (MgAlO) and acid (Nb2O5) catalysts, respectively, hindered internal ketones condense to form mostly dimers (2) in the presence of acid catalysts (entries 7–9). The formation of 2–5

Significance

The development of renewable liquid fuels and bioproducts is critical to reducing global reliance on petroleum and mitigating climate change, particularly for applications where few low-carbon alternatives exist. We combine chemical catalysis with life-cycle greenhouse gas (GHG) modeling to create a new platform for producing bioabased aviation fuel and automotive lubricant base oils. The recyclable catalysts we developed are capable of converting sugar and biomass-derived alkyl methyl ketones into cyclic enones via condensation reactions. These products can subsequently be hydrodeoxygenated to create a new class of aviation fuel and lubricant candidates with superior cold flow properties, density, and viscosity that substantially reduce GHG emissions relative to conventional petroleum.


Reviews included: J.A.D., University of Wisconsin–Madison.

The authors declare no conflict of interest.

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involves aldol-type condensations and Michael additions of ketone enolates or enols. Though the selectivity to 3 and 4 depends on the nature of the catalyst (acid/base), the pathway to 3 and 4 proceeds via 2 as an observable intermediate. Importantly, the reactivity of 1 also depends on the degree of steric hindrance near the reactive centers. Hence, the condensation of less-hindered methyl ketones proceeds smoothly at mild conditions (Table 1, entries 1–3, 5, and 6). The condensates (2–5) are finally hydrogenated to remove olefinic and carbonyl functionalities, as illustrated schematically in Table 1; this is accomplished in the liquid phase at 160 °C with 3.5 MPa of H₂ using Pt/NbOPO₄ (15) for 5–12 h to produce saturated alkanes 6–9 in yields as high as 99% (SI Appendix). For all of the condensation experiments, solvents such as toluene or cyclohexane are used as diluents to facilitate better understanding of the reaction. Practical application of such a process would use a reactive distillation setup and solvent-free conditions. Experiments conducted under such solvent-free conditions demonstrated that yields and selectivity comparable to those in Table 1 could be easily achieved through an optimization study (SI Appendix).

Next, we demonstrate the feasibility of producing jet fuel by cross-condensation of these methyl ketones to replicate the multicomponent mixtures of typical fuel blends. Reactions involving multiple synthons, such as a mixture of C₄–C₆ or C₆–C₇ methyl ketones, produced an array of trimer condensates (3), including those of intermediate carbon numbers (C₁₂–C₁₅ or C₁₂–C₂₁) resulting from all possible self-/cross-condensations (Fig. 1 and SI Appendix, Fig. S1). Encouraged by this finding, we evaluated key jet fuel properties of alkanes (7) derived from equimolar C₁–C₆ ketone synthons (SI Appendix, Fig. S2). The results (SI Appendix, Table S1) confirmed that (i) the cloud, pour, and freezing points are lower than −54, −46, and −100 °C, respectively. These measurements exceeded the equipment measurement limits and are far superior to currently available aviation biofuels. (ii) The volumetric energy density is 38.3 MJ/L and is also superior to typical aviation fuels. (iii) The boiling range is 198–302 °C, comparable to that of conventional jet fuel (148–280 °C). Therefore, by adjusting the concentrations of ketones, it is possible to produce mixtures of alkanes that mimic conventional jet fuel.

Table 1. Self-condensation of ketones in the presence of solid acid/base catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cₙ</th>
<th>R¹</th>
<th>R²</th>
<th>Catalyst</th>
<th>T, °C</th>
<th>Time, h</th>
<th>Conv. 1, %</th>
<th>Yields of condensates, %*</th>
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<td>2</td>
<td>C₆–C₇</td>
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<td>C₆–C₁₅</td>
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<td>61</td>
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</table>

Ketone (1, 2 mmol), catalyst (200 mg), and toluene (3 mL) was heated in a sealed Q-tube reactor. Conv. 1. Conversion of compound 1.

*Mixture of positional and stereoisomers.

†Catalyst MgAlO represents calcined Mg/Al-hydrotalcite (Mg/Al = 3:1) and Nb2O5 represents calcined niobic acid.

‡Cyclohexane (3 mL) was used as solvent.

Fig. 1. MgAlO-catalyzed cross-condensations of mixed ketone synthons and product distributions. Reaction conditions: a mixture of ketones (1, 2 mmol in total), catalyst (200 mg), and toluene (3 mL) was heated to 160 °C in a sealed Q-tube reactor for 5 h. (A) 2-butanone, 2-pentanone, and 2-hexanone (1.1:1:1.1:1). (B) 2-butanone, 2-pentanone, 2-hexanone, and 2-heptanone (1.0:1.0:1.0:1.1:1). (C) Simulated distillation curve for alkanes (C₁₂–C₁₈ and C₁₂–C₂₁) resulting from hydrodeoxygenation of condensates shown in A and B.
Petroleum refineries generate a variety of supplementary products vital to the transportation sector, including base oils used as lubricant blendstocks. The demand for synthetic lubricants (PAOs), produced from fossil-derived ethylene, also continues to grow due to their superior mechanical properties compared with conventional base oils, making them the benchmark for automobile lubricants (5); this inspired us to synthesize C_{30} to C_{45}-range molecules through self-condensation of ketones (1a-c) (SI Appendix, Table S1). Synthon 1a was obtained via monoalkylation of acetone with 2-ethylhexanol derived from Guerbet coupling of ethanol/1-butanol. Similarly, 1b was synthesized via monoalkylation of acetone with 1-octanol, which may further be produced from furfural and acetone (16). Finally, biomass-derived 2-methylfuran gave 1c (17). Ketones 1a-c underwent self-condensations to deliver the respective trimers (3a-c), which were then subjected to hydrodeoxygenation (SI Appendix) to obtain C_{33} and C_{45} alkanes (7a-c) in >97% isolated yields.

Our lubricant base oil molecules contain a cyclohexane ring and a quaternary carbon atom, and consequently represent a class of compounds that have not yet been tested as lubricants. We characterized these compounds by measuring their viscosity index (VI) and pour point and comparing them to those of conventional base oils and PAOs (SI Appendix, Table S2). All of the molecules synthesized showed excellent pour points (−51 to −69 °C) comparable to PAOs and far exceeding petroleum base oils, which have pour points in the −10 to −20 °C range. Thus, for most weather conditions, the compounds that we report here would be suitable in lubricant formulations. VI is a much more important property, a high VI indicating that the viscosity of the base oil does not change strongly with temperature, which is a desirable property for lubricant base oils and a strong motivation for using PAOs in formulations. Our studies show that the VI of 7b was very similar to that of PAOs (123 vs. 124) (18), whereas VIs of 7a and 7c compared well with those of mineral oil blendstocks (66 and 94 vs. 80–120). These test cases show only a glimpse of the possibilities for additional tribology research for lubricant applications, and developing an understanding between molecular structure and properties could unlock a new class of lubricants.

To quantify the carbon intensity of our lubricant and jet fuel production platform, we developed a model to simulate the process steps in a Brazilian sugarcane biorefinery and determine the life-cycle GHG footprint of potential products relative to their conventional petroleum counterparts. We modeled various pathways for producing drop-in jet fuel, lubricants, and ethanol using sucrose and bagasse-derived hemicellulose, with cellulose and lignin combusted for heat and power (Fig. 2). Through an integration of linear programming, process simulations, and life-cycle GHG modeling, we determined optimal allocations of sucrose and hemicellulose subject to different objective functions. We also explored the sensitivity of our results to uncertain variables (SI Appendix). In each case, we constrained biorefinery acetone and hydrogen imports/exports to zero to prevent the facility from relying on fossil inputs and eliminated the need to find local markets for excess acetone and hydrogen coproducts, which can be challenging in rural Brazil. We hypothesized that, although most individual pathways shown in Fig. 2 do not
satisfy this constraint, furanic and fermentative pathways could be combined in a single facility to balance processes that produce excess hydrogen and acetone with those deficient in them.

Maximizing the total reduction in annual GHG emissions achieved by the biorefinery (optimization A), assuming ethanol displaces gasoline, bioderived jet fuel displaces petroleum jet fuel, and bioderived lubricants replace PAO base oil, results in an advantage of 20% greenhouse gas (GHG) reductions relative to petroleum products. Needless to say, the commercial implementation of this technology would include financial implications that extend beyond GHG reductions; however, we hope that research such as that presented here will allow policymakers to create appropriate incentives to encourage optimal investments.

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