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Nikolay Shevchenko,[1] Jeremy Villafuerte,[1] Huitao Ling,[1] Christopher J. Walkling,[2] Derek D. Zheng,[2] Benjamin G. Harvey,[2] Mark Mascal*[1]

1. Department of Chemistry, University of California Davis, 1 Shields Avenue, Davis, CA 95616, United States
2. Research Department, Chemistry Division, US NAVY, NAWCWD, China Lake, California 93555, United States

Abstract

There is currently a demand for sustainable aviation fuel (SAF) that far exceeds supply. For this reason, a flurry of activity in the field of sustainable chemistry has centered around the development of workable technologies to convert biobased feedstocks into drop-in replacements for hydrocarbon fuels. Here, a simple, practical method is described that converts acetone, a biobased platform molecule that can be derived via multiple sustainable pathways, into a jet fuel that exceeds the specifications of commercial Jet A. The process involves dimerization of acetone to mesityl oxide, which is then processed in a biphasic, undivided electrochemical cell to give a combination of electrochemical coupling and condensation products. The resulting oxygenate is then hydrotreated to yield a mixture of highly branched alkanes and cycloalkanes.

Introduction

There are certain power requirements that can at present only be practically supplied by liquid fuels, the most evident of which is that which serves jet aviation. While other modes of transportation can be powered by motors that run on batteries or fuel cells, the extreme energy density constraints of air travel, particularly as it tends toward future supersonic and hypersonic capabilities, means there will be a role for tactical liquid fuels well into the foreseeable future. That said, the environmental impacts associated with deriving such fuels from petroleum are well understood, and multiple airlines are actively looking to source sustainable aviation fuel ("SAF") for their fleets.[1] This, along with growing consumer demand for sustainable products in general, has led to a strong upward trend in research activity in the renewable procurement of biobased chemicals.

One major obstacle to the adoption of biofuels has had to do with the integration of new products into the prevailing transportation infrastructure. Compatibility with existing engines is always going to be an issue, which can only be resolved by developing fuels that (1) inherently function within the present infrastructure, or (2) are "drop-ins" that are essentially identical to existing fuels. Novel fuels, particularly those for consumer automotive use, also face strict regulatory challenges. A second pain point is that fuels are a high-volume, low-margin commodity. This means that the capital costs of launching a new biobased fuel business are extraordinarily high and the runway to profitability is long. For these reasons, no biofuel production on anything like the scale practiced by the current oil companies has yet arisen. For this to happen, a technology would have to be developed that has virtually unlimited access to low-cost, biomass-derived feedstocks and does not entail prohibitive

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operating expenses. An analysis of the current sustainable approaches to biobased fuels suitable for aviation use reveals a "white space", where no technology can be seen to have secured commercial leverage.

While hundreds of papers have appeared on the synthesis of biofuels, they have many aspects in common. Since the major biomass fractions cannot generally be used directly as transportation fuels, some degree of processing is required. When carbohydrates and their derivatives are used, the first step is often a carbon-carbon bond forming reaction to get to a suitable carbon chain length, since common sugars have six or fewer carbons. This is followed by hydrodeoxygenation to bring the products down to the hydrocarbon oxidation state. Since carbohydrates are the most abundant biomass fraction, any viable future fuel industry would most likely be based around this "stitch and reduce" chemistry.[2]

Triacylglycerides, on the other hand, are already hydrocarbon-like and can be used as a diesel equivalent (biodiesel) after transesterification with methanol.[3] They can also be hydrodeoxygenated or hydrodecarboxylated to a drop-in for petroleum diesel, which can be submitted to cracking processes to tailor properties.[4] However, the higher cost and limited availability of plant oils, in addition to food-fuel controversies, weaken the argument for this approach.

Other biomass streams like lignin and extractives have also been advanced for biofuel production. The former in particular can be depolymerized and hydrogenated to give a complex mixture of phenylpropanoid-derived (C_{9+}) alkanes that may be useful in some fuel contexts, although the hydrogen burden of this method is high and no in-depth analysis of the fuel properties has been carried out.[5] In the same way, much work has been done on terpenoid extractives, the processing of which can lead to polycyclic hydrocarbons with remarkably high energy densities.[6,7] In this case, however, limited feed resources are a barrier to wider adoption as petroleum alternatives.

Paraffinic products have been made from biomass pyrolysis gas via Fischer-Tropsch or methanol-to-gasoline processes,[8] as well as by the refining of biomass derivatives (such as olefins from alcohol dehydration) using petrochemical technologies,[9,10] but such methods have not proven to be commercially viable at this point.[11]

Finally, wax ester, polyketide, and isoprenoid metabolic platforms have been exploited in the engineering of pathways for targeted microbial hydrocarbon production.[12,13] The closest these studies come to branched aliphatics is in the production of monoterpene (C_{10}) and sesquiterpene (C_{15}) products. However, most of the reported direct approaches to hydrocarbons have been proofs-of-concept and show low production efficiencies.[14]

One important property of finished hydrocarbon fuels is branching, which increases gasoline octane ratings. This can be clearly seen by the octane numbers associated with heptane (0) and 2,2,4-trimethylpentane (100). Branching and cyclicity are also important in jet fuel. Quoting a US Department of Energy report on Sustainable Aviation Fuel, "n-alkanes are acceptable but do not meet fluidity and handling properties, limiting their blend potential. Isoalkanes have high specific energy, good thermal stability, and low freezing points. Cycloalkanes bring complementary value to isoalkanes, providing the same functional benefits as aromatics by enabling fuels to meet the density requirement and potentially providing the seal-swelling capacity provided today from aromatics. Combined, iso-alkanes and cycloalkanes offer the potential to add value by enabling high energy density and minimizing emission characteristics."[15] Although some carbohydrate-to-fuel processes have given branched hydrocarbons by various means,[16] the great majority lead to linear or, at best, lightly branched products. In this work, we

describe the utility of acetone as a biobased feedstock for the straightforward production of isoalkanes and branched cycloalkanes using a simple and inexpensive process.

Biogenic acetone can be produced on industrial scales by three different methods. The first is the classic acetone-butanol-ethanol (ABE) fermentation performed by *Clostridia*.[17-19] This process is among the most mature biotechnologies and continues to evolve, and ABE yields of >120 g per kg of woody biomass have been reported.[20] Productivity is enhanced by continuous fermentation with gas stripping, where >100 g L^{-1} ABE has been achieved.[21,22] The coproducts, n-butanol and ethanol, are of course mainstream renewable chemicals and biofuels in their own right. Although practiced industrially throughout the mid-20th century, ABE technology has for the most part been supplanted by petrochemical routes to acetone. However, with the surge of interest in renewable chemicals, ABE is poised to make a comeback, with commercialization initiatives under active development.[23,24]

A second established method for the production of acetone is the ketonization of acetic acid. This can be either a gas-phase or aqueous-phase reaction and proceeds in high yields using a wide range of catalysts, including metal oxides and mixed metal oxides, hydrotalcites, and zeolites.[25,26] The acetic acid feed can be sourced by a range of sustainable technologies, including biogas processing,[27] aerobic fermentation of sugars,[28] or biomass pyrolysis (including hydrothermal methods) which generates acetic acid as a sizeable constituent of bio-oil.[29]

Finally, most of the acetone now produced industrially is as a byproduct of the oxidation of the petrochemical cumene to phenol. This same chemistry can also be performed on *p*-cymene, which yields *p*-cresol and acetone,[30] where the cymene can be sustainably derived from α-pinene, limonene, and other terpenes.[31]

Results and Discussion

While aldol self-condensation reactions of acetone have been known to give branched products, the reaction generates a mixture of low-octane hydrocarbons after hydrodeoxygenation.[32] We therefore considered that the reductive coupling of the acetone dimer mesityl oxide **1** would, in principle, give C$_{12}$ dimers only and at a lower initial oxidation state than condensation products. The concept is rendered graphically in Scheme 1. Thus, head-to-head, head-to-tail, and tail-to-tail dimerization would lead to highly branched intermediate products **2**-**4**, which ultimately could be reduced to **5**-**7**. In practice, the picture is significantly more complicated, as discussed below.
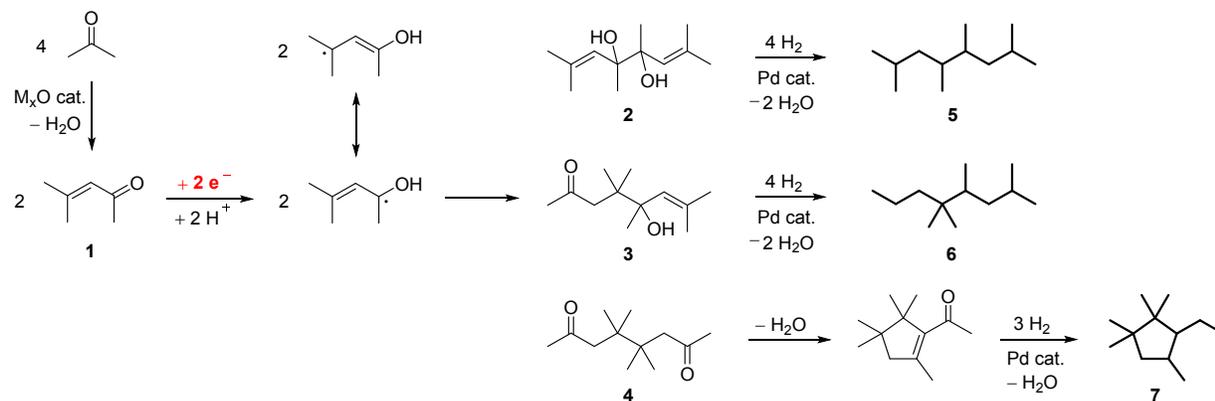
Scheme 1. Routes from mesityl oxide **1** to highly branched C$_{12}$ hydrocarbons **5**-**7**.

Electrochemistry is practiced industrially to supply a wide range of chemicals,[33,34] and is currently enjoying a renaissance as a clean synthetic method.[35] The electrochemical coupling of **1** was investigated in the mid-twentieth century to give products like **2**-**4**, although this involved the use of a divided cell with a mercury cathode and agar bridge operated at an elevated temperature, and no further processing of the electrolysis product was described.[36,37]

The cell we used to dimerize **1** is extraordinarily simple (Figure 1), involving only mesityl oxide layered over an aqueous sodium bicarbonate solution. Both electrodes are platinum, with the wire to the anode wrapped in Teflon extending below the phase boundary to avoid short circuiting. At the cathode, the mesityl oxide **1** can pick up an electron to form a radical which can dimerize to form C_{12} products. Since there is a direct interface between the cells, the resulting Na_2 dimer salt hydrolyzes to the intermediate products **2**-**4**, yielding back NaOH into the aqueous layer. An idealized balanced set of equations is given below. A significant advantage of an electroreductive approach is its low hydrogen burden. In the production of **5**-**7**, raw biomass is converted to saturated C_{12} fuels with the consumption of only 3-4 net molar equivalents of hydrogen. Compare this with the conversion of glucose to hexane, which requires 7 moles of H_2 per C_6 hydrocarbon.[38]
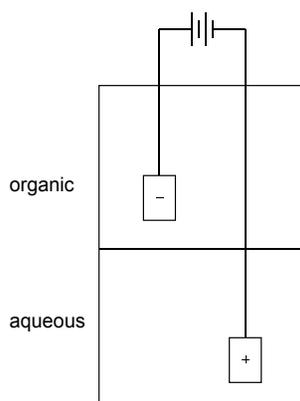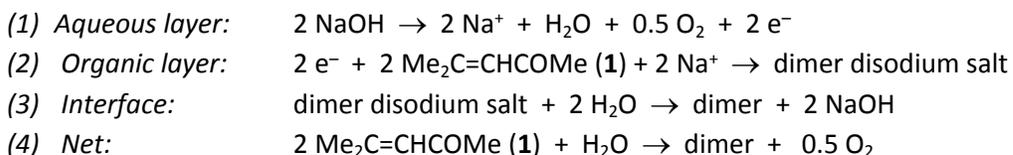

Figure 1. Undivided Pt//Pt cell for electrochemical coupling. This cell produces dimers by the hypothetical half reactions below. A 30 V commercial DC power supply was used, capable of operating at up to 10 amps. The process was operated at a constant potential of 15 V and an initial current of 0.15 A.

(1) *Aqueous layer:* $2\ NaOH \rightarrow 2\ Na^+ + H_2O + 0.5\ O_2 + 2\ e^-$
(2) *Organic layer:* $2\ e^- + 2\ Me_2C{=}CHCOMe$ (**1**) $+ 2\ Na^+ \rightarrow$ dimer disodium salt
(3) *Interface:*   dimer disodium salt $+ 2\ H_2O \rightarrow$ dimer $+ 2\ NaOH$
(4) *Net:* $2\ Me_2C{=}CHCOMe$ (**1**) $+ H_2O \rightarrow$ dimer $+ 0.5\ O_2$

In practice, the observed electrolysis product is broadly describable as a mixture of compounds containing **2**-**4** but considerably more complex (see Supplementary Information), with the additional complexity arising via an apparent combination of electrodimerization and condensation reactions, the latter made possible by direct contact between the mesityl oxide layer and the aqueous solution, which becomes increasingly basic as the electrolysis proceeds. Although a control reaction in the absence of current gave no product, the potential for trace water in the organic phase to be reduced to hydroxide

enables this competing pathway. In fact, mesityl oxide condensation dimers ("isoxylitones") have been described to occur alongside pinacol-type products in related reactions.[39,40]

Reduction of the mixed oxygenate was found to be best done in two steps; first a low-intensity hydrogenation over Pd/C catalyst to remove double bonds that were seen to be present, followed by hydrodeoxygenation over Pd/Al_2O_3 at 350 °C and 500 psi H_2. Final distillation of the product to remove the trace remaining oxygen content gave a clear, colorless, free-flowing liquid. The ^{1}H-NMR spectrum of this product showed the expected hydrocarbon signature, and ^{13}C NMR revealed a large number of peaks >32 ppm (the maximum chemical shift for linear alkanes), indicative of a high degree of branching (see Supplementary Information). Very small downfield peaks in both spectra suggest a minor olefinic or aromatic content, too small to quantify or characterize. Although both NMR and GC-MS indicated a complex mixture, four isomeric cycloalkanes of molecular formula $C_{12}H_{24}$ (unidentified in the NIST mass spectral library) together constituted the greater part of the sample (Figure 2). It should be noted here that mixtures are generally an advantage in jet and motor fuels, where hundreds of hydrocarbons may be present in commercial kerosines and gasolines.[41] The measured fuel analytics are given in Table 1, which show a favorable side-by-side comparison with the minimum specifications for Jet A.
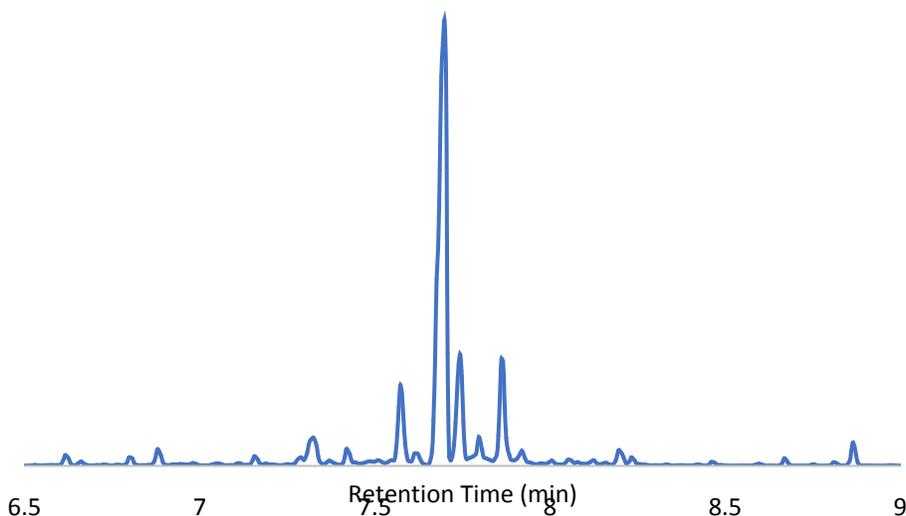

Figure 2. Gas chromatographic trace from finished hydrocarbon sample.

Table 1. Finished fuel analysis.

	Sample	Jet-A
Elemental Analysis	C, 85.65; H, 14.29	>13.5% H
Density @ 15 °C	0.803 g/mL	>0.775
Gravimetric net heat of combustion	43.37 MJ/kg	>42.8
Volumetric net heat of combustion	34.82 MJ/L	>33.2
Kinematic viscosity @ -20 °C	4.81 mm^{2}s^{-1}	<8.0
Kinematic viscosity @ -40 °C	10.75 mm^{2}s^{-1}	<12.0
Freezing point	<-55 °C	<-40 °C
Flash point	62 °C	>38 °C

Methods

Electrochemical dimerization

An undivided electrochemical cell was charged with a 5% aqueous sodium bicarbonate solution (50 mL) over which was carefully layered mesityl oxide (24.0 mL, 20.6 g, 0.210 mol) containing tetrabutylammonium tetrafluoroborate (1.0 g). A platinum cage cathode was situated in the organic phase, and a platinum plate anode, insulated from the organic layer by a Teflon sleeve, was extended into the lower aqueous phase. A magnetic stir bar was added and gentle stirring was started. Electrolysis of this biphasic mixture was performed at 0.15 A/15 V at 0 °C. Over the course of 12 h, the current gradually dropped to 0.04 A, at which point conversion was 30% by GC as measured against an $n\text{-}C_{12}H_{30}$ internal standard. The organic phase was separated and the water layer was additionally extracted with ether (50 mL). The combined organic phases were dried over magnesium sulfate and filtered through the Celite. The ether was evaporated to give a yellow liquid (18.9 g). The unreacted mesityl oxide was removed by distillation at 12 Torr and the crude electrolysis product (7.1 g) was used directly in the next step.

Intermediate hydrogenation over Pd/C

A 300 mL Parr Instruments Hastelloy pressure vessel was charged with the product mixture from seven combined electrochemical dimerization runs as described above (47.0 g), along with ether (50 mL), 5% Pd/C (0.50 g), and a magnetic stir bar. The vessel was purged twice with hydrogen gas and then pressurized to 200 psi H_2. After stirring at room temperature for 3 h the reaction mixture was filtered through Celite and the solvent was removed by rotary evaporation. The residue was vacuum distilled and a wide fraction was collected (bp 64-91 °C at 0.2 Torr) to give 37.7 g (80.2% mass recovery) of a colorless liquid product.

Final hydrogenation over Pd/Al$_2$O$_3$

A 300 mL Parr Instruments Hastelloy pressure vessel was charged with the product mixture from the previous step (37.0 g), along with 5% Pd/Al$_2$O$_3$ (1.8 g) and a magnetic stir bar. The vessel was purged twice with hydrogen gas and then pressurized to 500 psi H_2. Stirring was started and the reactor was heated to 350 °C. After 12 h the reaction was cooled to room temperature and diluted with ether (100 mL). The resulting mixture was filtered through Celite and the ether was removed by rotary evaporation to give a colorless liquid product (30.4 g, 82.2% mass recovery). A sample of this material (26.3 g) along with calcium hydride (0.25 g) was introduced into a round bottomed flask and distilled by short path distillation (6.1 Torr, bath temperature, 75 °C; head temperature, 55-60 °C). The sample was collected in 5 fractions. The first fraction (1.2 g) was discarded. The following four fractions (total mass of 20.9 g, 79.4% recovery) were combined and analyzed (see Supplementary Information for methods).

Conclusion

The work described in this paper may, on one hand, be considered a valorization of the ABE fermentation. Ethanol and butanol have their own dedicated fuel markets, and can be converted into ethylene and butene, which are cornerstones of the petrochemical industry. Acetone, on the other hand, is not a suitable fuel in its own right due to its volatility, reactivity, low energy density, and

incompatibility with engine seals, so its primary use is as an industrial solvent. As shown here, it can be inexpensively converted into high-performance jet fuel. From another perspective, the SAF market is enormous, and the current production capacity provides only a fraction of the demand. Given that practically unlimited quantities of acetone could become available via one or more of three industrial-scale routes, *i.e.* via ABE fermentation, ketonization of acetic acid, and *p*-cymene oxidation, this study may provide the basis for a viable commercial path to SAF. The technology is extraordinarily simple, and further streamlining of the reduction process into a single unit operation (work in progress) would provide a path to an immediately deployable SAF in as few as three steps from a biobased feed. Recent technical innovations involving advanced electrode configurations and the use of non-noble metal electrodes for sustainable synthesis also provide opportunities to further refine the technology.[42,43]

Author contributions

Mascal: conceptualization, funding acquisition, project administration, supervision, writing – original draft, writing – review and editing

Shevchenko, Villafuerte, Ling: investigation, methodology, writing – review and editing

Harvey: supervision, formal analysis, writing – review and editing

Walkling: investigation

Zheng: formal analysis

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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