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COMMUNICATION

Synthesis of Aviation Fuel from Bio-Derived Isophorone

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Using photochemical [2+2] cycloaddition, a cyclobutane dione was generated from isophorone, a condensate of bio-acetone. Hydrodeoxygenation of the dione yielded a mixture of polycyclic alkanes, whose high energy density is appropriate for high perfomance aviation applications. This work outlines a light-based approach to increase the energy density of a potential renewable carbon aviation fuel in high yields and high carbon efficiency without sacrificing performance.

The formulation of bio-derived fuels is a means to mitigate the harmful environmental impacts of the transportation sector. In particular, the use of renewable fuels will alleviate the depletion of global fossil fuel supplies, sequester CO_2 through photosynthesis, minimize the accumulation of anthropogenic greenhouse gases in the atmosphere, and can reduce emissions of particulates and other pollutants.[1-4] In order for such a fuel to be impactful, it must either be cost-competitive or provide a performance advantage that incentivizes stakeholders to move away from traditional petroleum fuels. One such performance advantage is an increased energy density, which can extend the range or raise the payload of a vehicle or aircraft. Thus, the search for new performance advantaged, bio-derived fuels is vitally important to ensure future transportation needs while preventing further deterioration of the environment. In the case of aviation fuels, stringent specifications (ASTM D1655 and ASTM D7566)[5,6] are in place to ensure the safe operation of new fuels in existing engines, adding yet another challenge to the introduction of renewable options.

Acetone is a useful bio-derived building block that can be produced by several routes, and recently the acetone-butanol-ethanol (ABE) fermentation process has renewed interest as a pathway to generate bio-derived fuels.[7] In this process, sugars are converted into acetone, butanol, and ethanol, typically in a 3:6:1 ratio,[8] by solventogenic *Clostridium* bacteria. Upgrading of an ABE fermentation broth via chain-extension and hydrodeoxygenation steps furnished bio-derived ketones that are potential fuel precursors, with 38% carbon yield for C_7 to C_{15} ketones.[9,10] Moreover, new technologies based on advances in genetic engineering combined with alternative fermentation techniques, namely mixotrophy, significantly increase the direct production of acetone and can prevent the loss of carbon as CO_2, a substantial challenge in traditional ABE fermentations.[11] These new technologies significantly improve the economics of bio-acetone and thus have the potential to successfully elevate its use as a bio-derived starting material for chemicals and fuels production.

There are many challenges in using acetone for fuels applications. Its volatility precludes it from direct use as a fuel and it requires chemical upgrading to be suitable for introduction into the fuel supply. Acetone is also a strong solvent and incompatibility with engine components and seals has been an additional barrier to its use in current engines. Previous work in our group demonstrated, however, that acetone can be upgraded through aldol condensation reactions and selective reductions to branched drop-in gasoline and diesel replacements.[12] Acetone can also be condensed to generate isophorone, which is a substituted cyclohexene, providing another potential route to energy dense fuels. Recently, the mild, industrially friendly, and economical conversion of acetone to isophorone with calcium carbide was published, demonstrating a hydrogen-free method of upgrading a bio-derived feedstock.[13,14] The product of isophorone hydrodeoxygenation[15] – 1,1,3-trimethylcyclohexane – and dimers of isophorone[16] have also been claimed as high energy density fuel but without actual quantification of their energy content. Substituted cyclohexanes from the aldol condensation of isophorone and furanic aldehydes have high energy densities (around 43 MJ/kg) and may be appropriate for aviation applications.[17]

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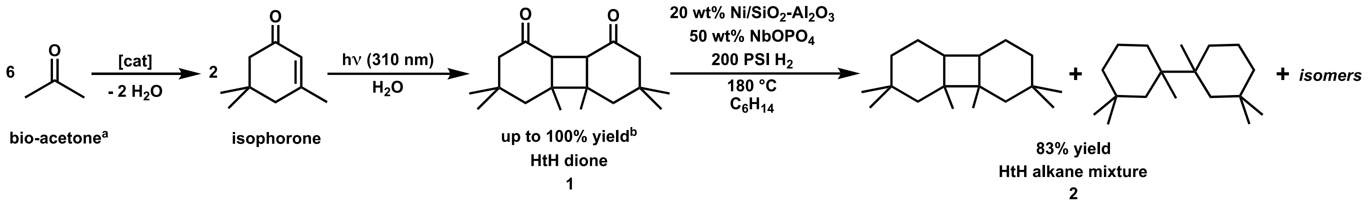

Figure 1 Synthesis of **2** from isophorone. [a]The condensation of acetone to isophrone was not completed with this work. Ref. 13 and 14 [b]Ref 27.

This report further investigates the upgrading of acetone via isophorone, with particular focus on energy dense aviation fuel. By utilizing isophorone as a renewable feedstock to synthesize fuels, the hydrogen demand of the overall process is reduced, compared to other bio-derived feedstocks that require extensive hydrotreating to remove oxygen content. Reducing hydrotreatment in the synthesis of renewable fuels is an important consideration because most hydrogen is derived from steam reforming of natural gas and generates CO_2.[18]

The composition of Jet-A varies widely depending upon the petroleum source, but is generally comprised of aromatics, cycloalkanes, and linear and branched alkanes.[19,20] Because of the large fraction of cyclic alkanes in Jet-A, which have higher gravimetric and energy densities compared to their linear and branched congeners, and because cyclobutanes have been proposed for high energy density fuel applications,[21,22] we explored the synthesis of a polycyclic cyclobutane from isophorone. Polycyclic species, particularly those with considerable ring strain, are expected to have much higher energy content than unstrained systems with similar molecular weights, making strained systems well-suited for high energy density applications.[21,23-26] The characterization and fuel properties of the strained cyclobutane system are reported herein.

The photochemical [2+2] cycloaddition of isophorone to generate the desired cyclobutane moiety was explored because of its high atom-efficiency, mild reaction conditions, and thoroughly explored photophysics (Figure 1).[27-31] Isophorone is an apt substrate for this [2+2] transformation because of its enone functionality, which allows for the absorption of longer wavelengths of light (greater than 310 nm) and circumvents the need for a photosensitizer. A similar strategy, wherein the photochemical [2+2] addition of isophorone and bio-derived olefins generated a series of cyclobutanes, was recently reported,[32,33] highlighting the utility of photochemistry in synthesizing new energy dense fuels.

In this work, the photochemical [2+2] coupling of isophorone is high yielding, selective for the head-to-head (HtH) isomer of the dione, and can be performed in water. The yield is quantitative when completed on scales of less than half a gram.[30,31] The reaction is amenable to scale up without loss of selectivity, but the yield is lowered, particularly with shorter irradiation times. The [2+2] addition product precipitates from solution as a white powder, allowing for facile isolation of the desired product. Upon filtration, the aqueous filtrate containing residual isophorone can be reused, thereby improving the overall yield of the cycloaddition.

Isolation of the HtH dione (**1**) was followed by hydrodeoxygenation to yield the corresponding alkane, whereby the solid dione was converted to a mixture of liquid alkanes. The use of Ni/Al_2O_3-SiO_2 (20 wt%) and $NbOPO_4$ (50 wt%) with heating to 180 °C under H_2 pressure (200 PSI) for 16 h, similar to conditions previously developed by our group for the hydrodeoxygenation of ketones,[12,34] furnished a mixture of alkanes (HtH alkane mixture (**2**); Figure 1) in 83% isolated yield. Analysis of the mixture by GC-MS revealed isomers of the desired cyclobutane and isomers of the ring-opened species (Figure S3). Quantification of the cyclobutane and ring-opened products was performed by GC-FID and determined to be 91.2% and 8.8%, respectively (Table S1).

The fuel properties, which include kinematic viscosity, density, specific energy, energy density, surface tension, boiling point, freezing point, flash point, and effective smoke point (ESP), of **2** were analyzed and compared to those of Jet-A to determine the suitability of the mixture as an aviation fuel (Table 1). The kinematic viscosity (at −20 °C) of the cyclobutane mixture, 469.35 mm^2/s, exceeds the specification for aviation turbine fuel (< 8 mm^2/s; ASTM D1655)[5]. We also examined the properties of the alkane mixture blended with Jet-A (POSF

Table 1 Summary of fuel properties of **2**, Jet-A (POSF 10325), their blends, and **3**.

Entry	Sample	Viscosity (-20 °C; mm^2s^{-1})	Density (25 °C; g/mL)	Energy Density (MJ/L)	Specific Energy (MJ/kg)	Flash Point (°C)	ESP (mm)	Surface Tension (mN/m)
1	**2**	469.35	0.897	38.0	42.4	78.5	16.3	29.0
2	Jet-A (POSF 10325)	4.47	0.796	34.0	42.7	47.0	20.9	24.2
3	10% v/v blend	5.52	0.806	34.4	42.7	49.0	20.0	24.3
4	20% v/v blend	6.90	0.816	34.8	42.6	51.0	19.2	24.2
5	30% v/v blend	8.74	0.827	35.3	42.6	53.0	18.5	24.5
6	**3**	2.46	0.779	33.0	42.3			

10325)[35] at 10%, 20%, and 30% v/v to see how blending affects the viscosity and because the myriad specifications of Jet-A make a single component renewable replacement unlikely. The viscosities of the 10% and 20% blends were within the specifications of Jet-A, while the viscosity of the 30% blend was above the maximum limit at 8.7357 mm^2/s.

The viscosity, density, and surface tension of a fuel influence its atomization and ignition and thus are important considerations when formulating a drop-in fuel that needs to perform in existing engine infrastructure.[36,37] The density of **2** was 0.897 g/mL, significantly higher than that of Jet-A (POSF 10325), 0.796 g/mL, and the range given in the specification (0.775 to 0.840 g/mL). Upon blending, the density increased linearly relative to Jet-A with increasing percentage of **2**, as expected (Table S2). Moreover, the density of the blends did not exceed the upper limit of the specification, with the highest density belonging to the 30% blend at 0.827 g/mL. The surface tension of **2** was 29.0 mN/m, compared to 24.21 mN/m for Jet-A. The blends were within error of that of Jet-A, with surface tensions ranging from 24.2 to 24.5 mN/m.

The energy density, which is an important consideration for volume-limited fuels applications, and the specific energy, which is considered for weight-limited or single-use applications, were measured for **2** and its blends with Jet-A. The energy density of **2**, as measured by bomb calorimetry, was 38.0 MJ/L. This was significantly higher (12%) than the measured energy density of Jet-A, 34.0 MJ/L (specification ranges from 33.2 to 36.0 MJ/L) and consistent with that of a previously published cyclobutane derived from isophorone.[32] With increasing blending, the volumetric energy content of Jet-A increased. The 30% blend had the highest energy density of the blends and improved that of Jet-A by 3.8%. The specific energy of **2** was 0.3 MJ/kg, 0.7 % lower than that of Jet-A, and when blended the specific energies were within error, demonstrating that blending did not significantly change the specific energy. In contrast, the energy density of the blends rose with increasing percentage of **2** because of the corresponding increase in density of the blends.

In order to more fully understand the impact of the cyclobutane moiety on the energy content of **2**, the analogous monomer, 1,1,3-trimethylcyclohexane (**3**) was synthesized. Using similar hydrodeoxygenation conditions to the dimeric species, **3** was furnished from isophorone (see SI). While the specific energy of **3** was similar to that of **2**, the energy density was much lower. Moreover, the density of **3** was significantly lower than that of **2** (13%), which likely contributed to the large difference in the energy density and highlights the advantage of dimerization. The benefit of dimerization is also seen in the plot of the energy density versus the specific energy (Figure 2).

The flash point and boiling point of a fuel are used to evaluate its fire safety during storage and handling.[38,39] **2** had a high flash point, at 78.5 °C. The specification of Jet-A requires a minimum flash point of 38 °C and was measured to be 47.0 °C for our sample. Moreover, the measured flash point of **2** exceeded that of the JP-5 specification (minimum 60°C)[40]; JP-5 is formulated to have improved flash point for aircraft carrier applications. Blending **2** with Jet-A improved the flash point, with an increase of 2 °C for every 10% increase in blending. The boiling point of **2**, which ranged from 278 to 302 °C, was measured by a simulated distillation method on GC-MS.[41] These values were within the specification of Jet-A.

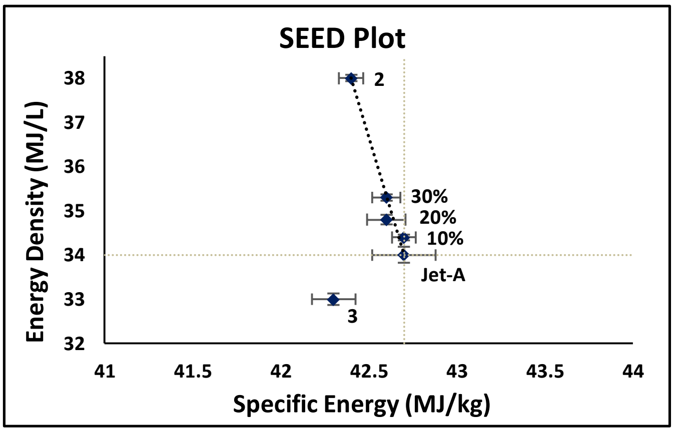

Figure 2 Specific Energy-Energy Density (SEED) plot comparing the energy density and specific energy of **2**, Jet-A, the volumetric bends, and **3**.

A freezing point below −40 °C is required for Jet-A because of the high altitude and low temperature conditions under which aircraft operate. The freezing point of each sample was measured by DSC. **2** freezes below−80 °C. The Jet-A sample and its blends all had freezing points below −40 °C, confirming their suitability for low temperature applications.

The smoke point (SP) indicates the tendency of a fuel to form carbonaceous soot particulates when burned; ASTM D1655 requires that SP > 18 mm for Jet A.[5] (Smoke point is inversely related to sooting tendency, so larger values correspond to cleaner burning fuels.) However, the standard ASTM D1322 smoke point test requires 10 mL of sample,[42] which was excessive for this study, so instead sooting tendency was measured with a yield-based method and then converted to effective smoke point (ESP),[43] as discussed in the ESI. The ESP of **2** was 16 mm, which is worse than the Jet A (20.9) and does not meet the standard. However, the ESP of the blends all exceeded 18 mm and therefore meet the standard. The high sooting tendency of **2** is likely a consequence of its high molecular weight, multiple rings, and methyl side-chains.[44-46]

While the high energy density of **2** was suitable for improving the performance of Jet-A with blending, its high viscosity limited the blending to 30% by volume. It was demonstrated, however, that blending **2** with Jet-A greatly improved the energy density without compromising the specific energy which may be more applicable to specialized volume limited applications. In this case, the incorporation of renewable carbon, furnished through facile synthetic steps starting from fermentation broth, delivered increased performance to the petroleum-based conventional fuel. This improvement highlights a route to lower the environmental impact of the aviation industry through bio-derived drop-in fuels. In particular, the use of unsaturated bio-derived building blocks to synthesize strained cyclobutanes is a potential path to develop energy dense renewable fuels; however, further testing is necessary to ensure engine compatibility and performance in aircraft.

Conflicts of interest

There are no conflicts to declare.

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