Electronic Supplementary Information for:

Synthesis of Aviation Fuel from Bio-Derived Isophorone

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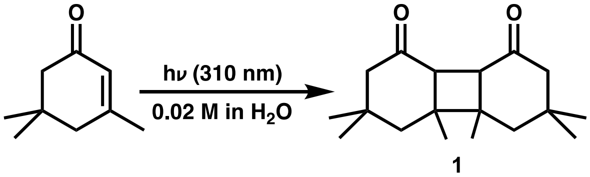
General considerations.

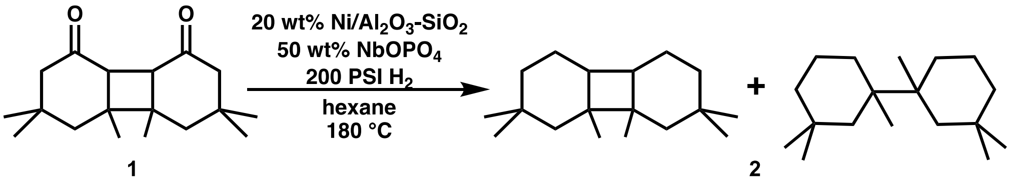
All chemicals and solvents were obtained from commercial sources and used as received unless otherwise specified. $NbOPO_4$ was heated to 100 °C in a vacuum oven overnight prior to use. Jet-A was received from Dr. Tim Edwards at the Air Force Research Laboratory (POSF 10325). Photochemical reactions were completed with a 450 watt Hanovia medium pressure mercury-vapor lamp submerged in a quartz chiller well maintained at 15 °C with a recirculating chiller. ^{1}H and ^{13}C NMR spectra were collected at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts referenced to the residual solvent signal. GC-MS analysis was carried out using an Agilent 7890 GC system equipped with an Agilent 5975 mass selective detector (MSD), a flame ionization detector (FID), and a Polyarc system. The Polyarc system is a catalytic microreactor that converts all organic compounds to methane after chromatographic separation and prior to detection. Combustion calorimeter measurements were performed using an IKA C1 compact combustion calorimeter. Higher heating values were measured in quadruplicate and averaged. The lower heating values (reported as the specific energy) were calculated by subtracting the contribution due to hydrogen content from the higher heating value. Differential scanning calorimetry (DSC) measurements were performed using a Netzsch DSC 204 F1 Phoenix with a Netzsch CC300 LN2 cryostat in sealed aluminum pans. Flash point was measured on an Anton Paar PMA-5 Pensky-Martens flash point tester according to ASTM D93. Viscosity and density measurements were performed using an Anton Paar SVM 3001 according to ASTM D7042 and D4052. Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, GA, USA). Surface tension was measured with a DataPhysics DCATS15 instrument with module DCATS 31. Effective smoke point (ESP) measurements were completed by Dr. Charles McEnally and Junqing Zhu at Yale University.

[2+2] Cycloaddition to make the HtH dione (1).



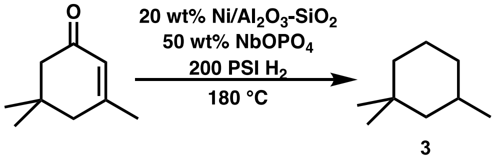
The [2+2] cycloaddition of isophorone to generate the head-to-head dimer was performed using a modified literature procedure.[1,2] Isophorone was weighed into a 20 mL scintillation vial (10.00 g; 0.07236 mol) and divided between two 500 mL Pyrex Erlenmeyer flasks filled with water, making two dilute solutions (~0.07 M). These solutions were irradiated overnight with a 450 W medium pressure mercury vapor arc lamp. The white solid that had deposited along the walls of the flasks was collected by filtration and washed with water. The solid was eluted into a clean filtration flask with dichloromethane (~30 mL) and dried over $MgSO_4$. Solvent was removed under reduced pressure, yielding a pale yellow, oily solid, which was washed with diethyl ether to furnish a white solid (1.00 g; 0.00362 mol; 10% yield). Spectroscopic analysis of the product matched previously published data.[2] The initial aqueous filtrate could be reused, with the addition of more isophorone, to improve yields (to 20-30%) and make the process more sustainable. The aqueous filtrate was reused up to 5 times.

Hydrodeoxygenation of 1.



A 50 mL stainless-steel reactor was charged with the **1** (0.750 g; 0.00271 mol), Ni/Al_2O_3-SiO_2 (20 wt %; 0.150 g), $NbOPO_4$ (50 wt %; 0.375 g), and 12 mL hexanes. The reactor was sealed and pressurized with 200 PSI H_2, flushing three times. The vessel was placed in a preheated aluminum block at 180 °C and heated for 16 h with stirring. The reactor was cooled in a water bath until reaching room temperature and depressurized. An aliquot of the resulting mixture was filtered and analyzed by GC-MS to confirm complete consumption of the **1** and formation of alkane products. The reaction mixture was filtered through a silica plug and solvent was removed under reduced pressure, yielding a colorless liquid (0.622 g; 0.00225 mol; 83% yield). The ratio of cyclobutane and ring-opened isomers, 91.2% and 8.8%, respectively, were determined by GC-FID. The ^{1}H and ^{13}C NMR spectra were collected, but because of the complexity of the alkane mixture, they were not fully analyzed. The ^{1}H NMR spectrum is consistent with a mixture comprised solely of alkanes. The ^{13}C NMR spectrum contains over 200 resonances, likely from the 13 different isomers observed by GC-MS.

Preparation of 1,1,3-trimethylcyclohexane (3).



A 50 mL stainless-steel reactor was charged with isophorone (2.00 g; 0.0145 mol), Ni/Al_2O_3-SiO_2 (20 wt %; 0.400 g), and $NbOPO_4$ (50 wt %; 1.00 g). The reactor was sealed and pressurized with 200 PSI H_2, flushing three times. The vessel was placed in a preheated aluminum block at 180 °C and heated for 24 h with stirring. After 5 h the H_2 pressure had dropped significantly, and the reactor was repressurized to 200 PSI The reactor was cooled in a water bath until reaching room temperature and depressurized. Two 5 mL portions of diethyl ether were added to transfer the reaction mixture to a 20 mL scintillation vial. The resulting mixture was filtered over a pad of Celite and an aliquot was analyzed by GCMS, showing complete conversion to the desired alkane. The product was isolated by concentrating the diethyl ether solution under reduced pressure (1.10 g, 0.00872 mol, 60%). The ^{13}C NMR spectrum was consistent with a previously published spectrum.[3] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.65 – 0.79 (m, 2H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 6H), 1.03 (td, *J* = 13.2, 4.5 Hz, 1H), 1.32 – 1.64 (m, 6H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 22.71, 23.26, 24.96, 28.46, 31.07, 33.70, 35.49, 39.24, 48.90.

Figure S1. ^{1}H NMR spectrum of the **2** (CDCl$_3$; 25 °C).

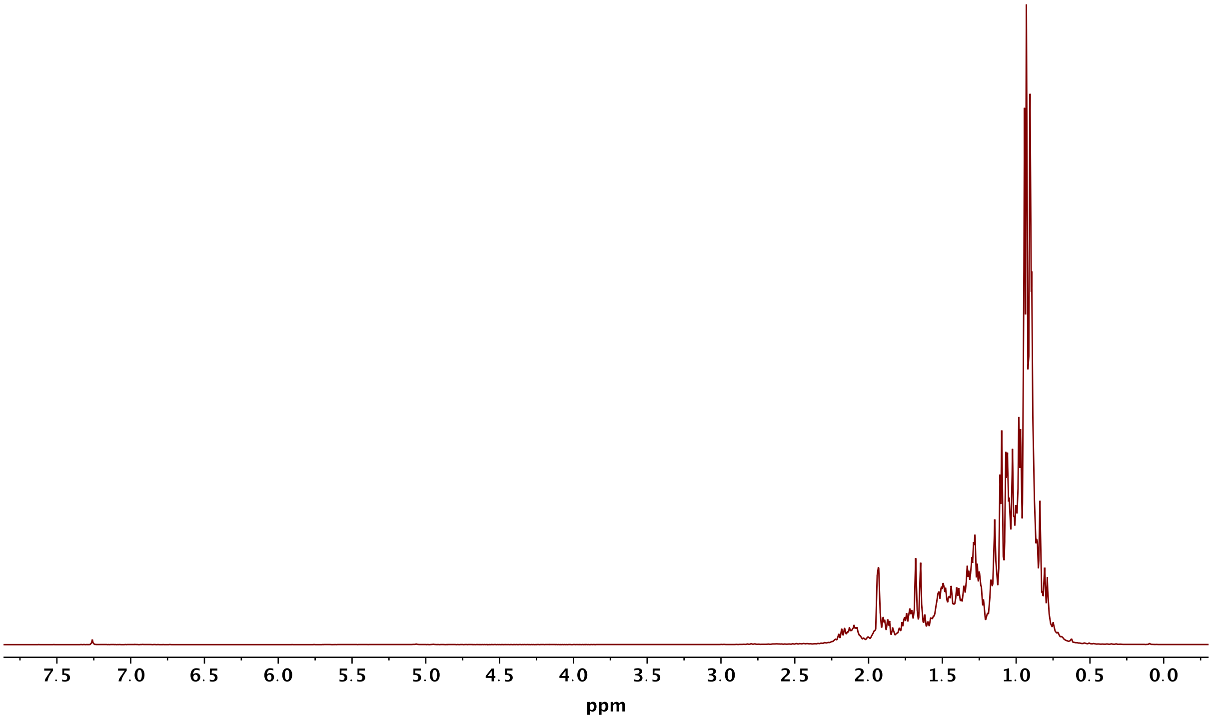


Figure S2. ^{13}C NMR spectrum of **2** (CDCl$_3$; 25 °C).

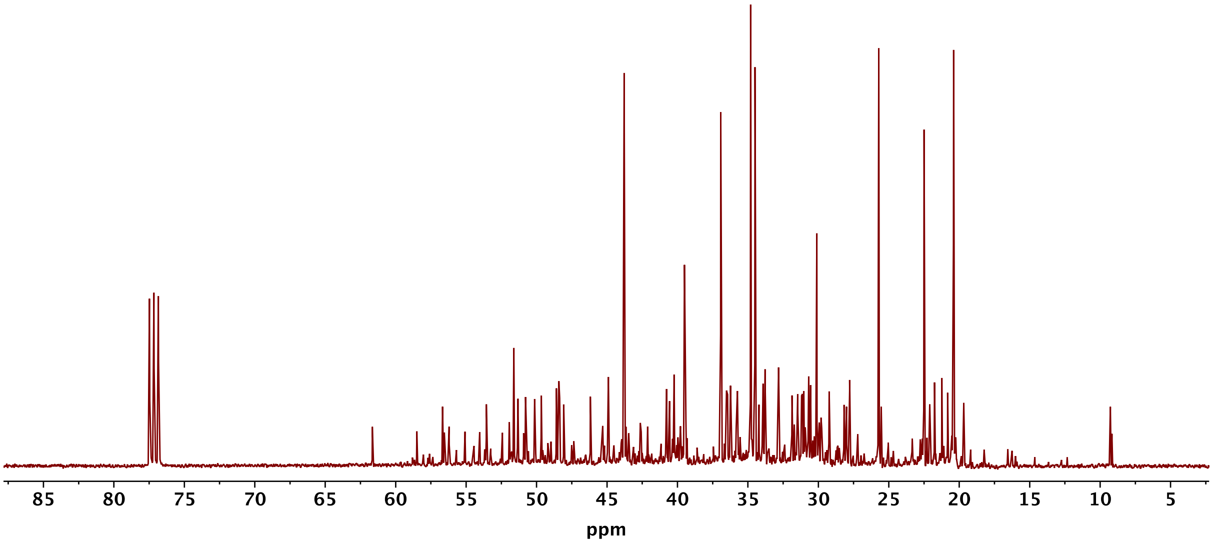


Figure S3. GC-MS trace of **2**.

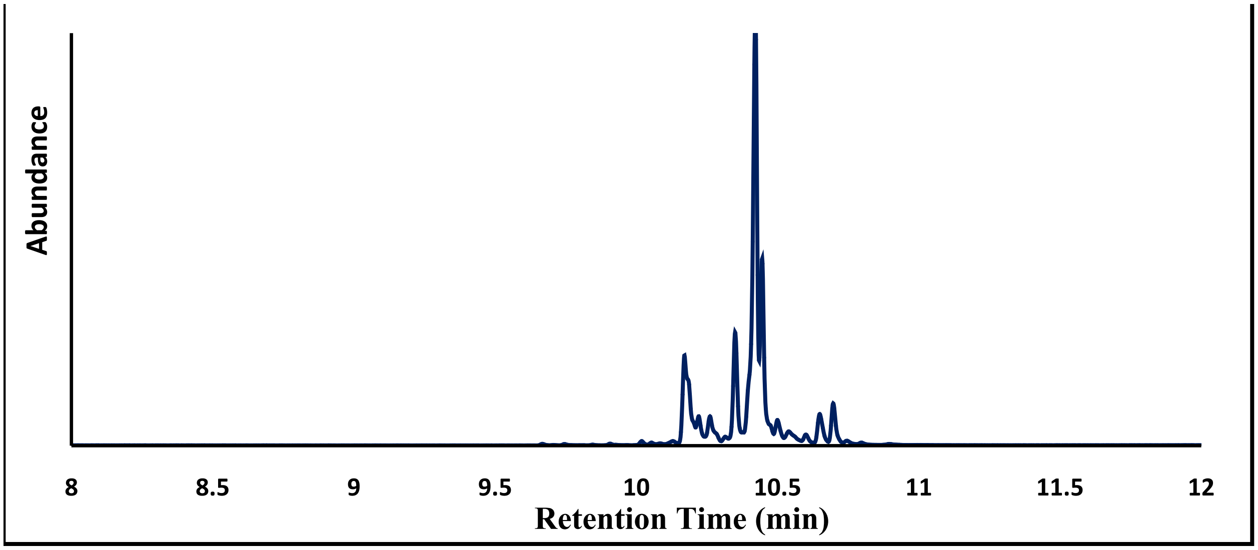


Table S1. Analysis of GC-MS trace of **2**.

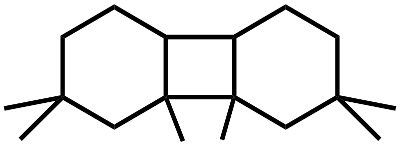
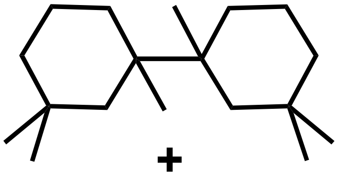
	m/z	Retention Time (min)	Mass %
	248	10.028 10.138 10.181 10.325 10.360 10.431 10.455 10.510 10.660 10.708	91.2%
 + *isomers*	250	10.230 10.271 10.611	8.8%

Figure S4. ^{1}H NMR spectrum of **3** ($CDCl_3$; 25 °C).

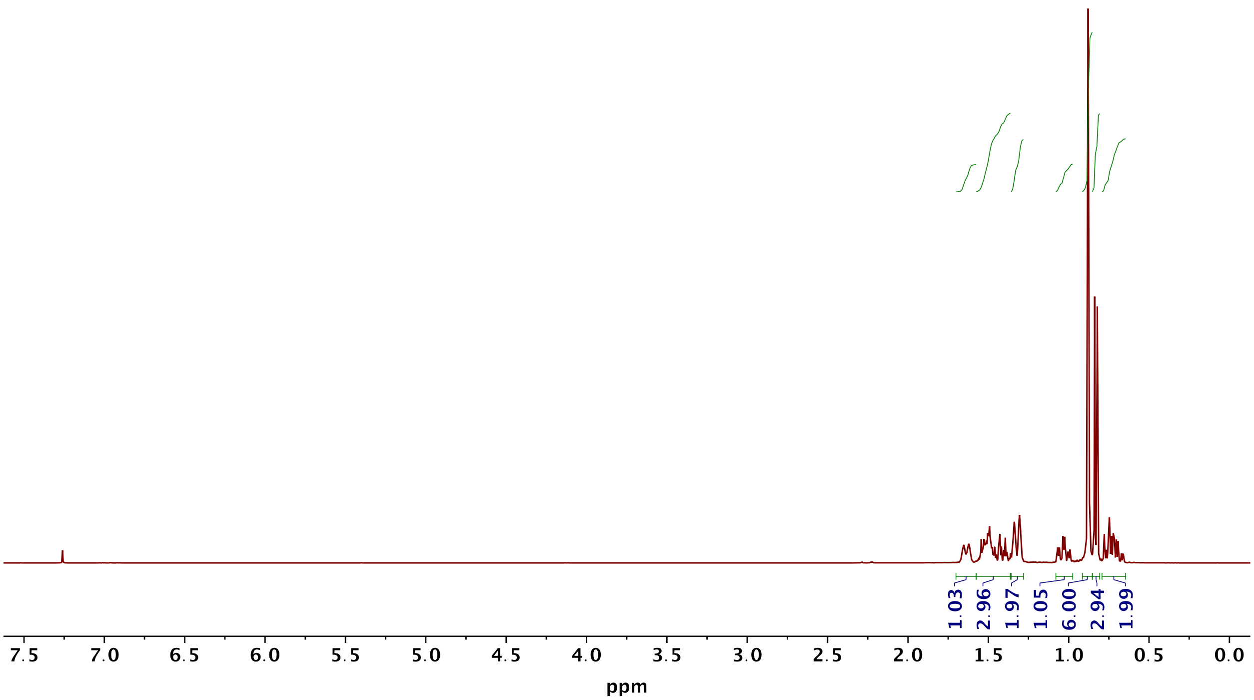


Figure S5. ^{13}C NMR spectrum of **3** ($CDCl_3$; 25 °C).

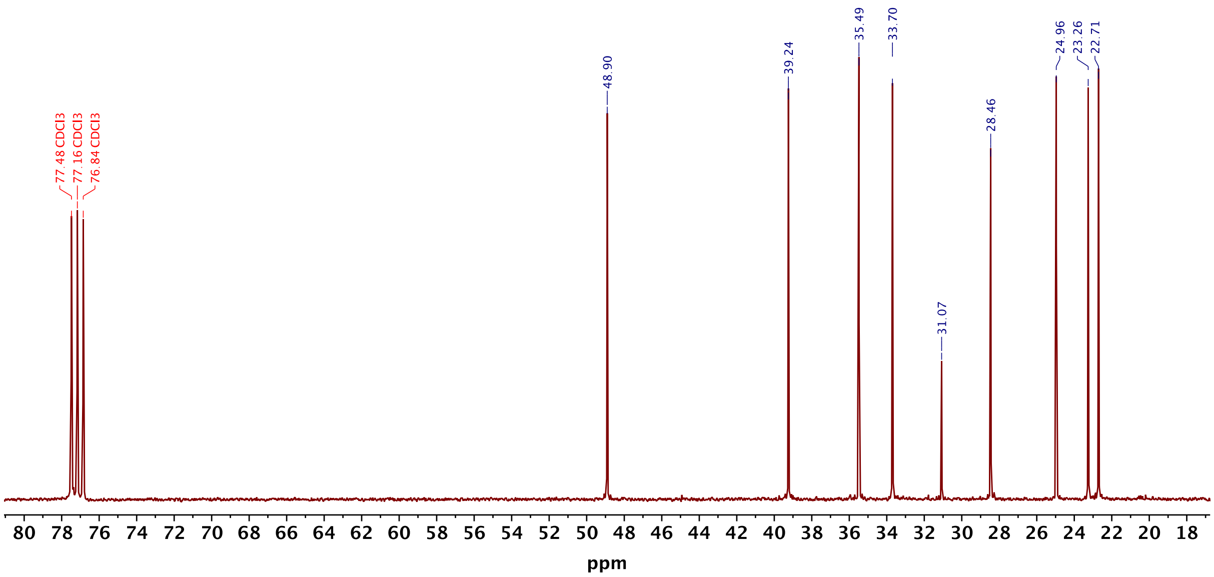


Table S2. Density and kinematic viscosity of **2**, Jet-A, and blends.

Sample	Temperature (°C)	Density (g/mL)	Kinematic Viscosity (mm^2/s)
2	-40	0.94072	11399
	-20	0.92689	469.35
	-5	0.91677	109.83
	10	0.90679	39.552
	25	0.89690	18.630
	40	0.88705	10.484
Jet-A	-40	0.84461	9.3596
	-20	0.82917	4.4711
	-5	0.81802	3.0094
	10	0.80692	2.1816
	25	0.79584	1.6700
	40	0.78468	1.3322
10% v/v blend	-40	0.85443	12.312
	-20	0.83925	5.5176
	-5	0.82823	3.6004
	10	0.81724	2.5475
	25	0.80626	1.9166
	40	0.79526	1.5046
20% v/v blend	-40	0.86424	16.763
	-20	0.84919	6.9008
	-5	0.83827	4.3172
	10	0.82736	2.9684
	25	0.81648	2.1745
	40	0.80558	1.6799
30% v/v blend	-40	0.87424	22.873
	-20	0.85939	8.7357
	-5	0.84858	5.2563
	10	0.83780	3.4980
	25	0.82706	2.5080
	40	0.81631	1.8967

Table S3. Density and kinematic viscosity of isophorone and **3**.

Sample	Temperature (°C)	Density (g/mL)	Kinematic Viscosity (mm^2/s)
isophorone	0	0.93878	5.1381
	10	0.93043	3.8324
	25	0.91885	2.6459
	40	0.90707	1.9567
3	-40	0.83073	4.0688
	-20	0.81468	2.4553
	-5	0.80271	1.8443
	10	0.79089	1.4454
	25	0.77936	1.1673
	40	0.76724	0.9694

Table S4. Specific energy, elemental composition, and energy density measurements.

Sample	Specific Energy (MJ/kg)	%C	%H	Energy Density (MJ/L)
2	42.421(70)	87.09	12.88	38.0
Jet-A	42.671(180)	85.61	13.94	34.0
10% v/v blend	42.652(67)	85.93	13.72	34.4
20% v/v blend	42.461(110)	85.66	13.70	34.8
30% v/v blend	42.600(79)	86.29	13.41	35.3
Isophorone	35.293(131)	74.97[a]	8.39[a]	32.4
1	35.555(100)	78.21[a]	10.21[a]	[b]
3	42.292(124)	85.63[a]	14.37[a]	33.0

[a] value was not determined experimentally

[b] value was not calculated – **1** is a solid

Table S5. Surface tension and freezing point measurements.

Sample	Surface Tension (mN/m)	Freezing Point (°C)
2	28.97(35)	< -80
Jet-A	24.21(3)	-43.3
10% v/v blend	24.32(6)	-46.9
20% v/v blend	24.24(4)	-44.3
30% v/v blend	24.48(28)	-47.3

Figure S6. Specific energy versus blending percent.

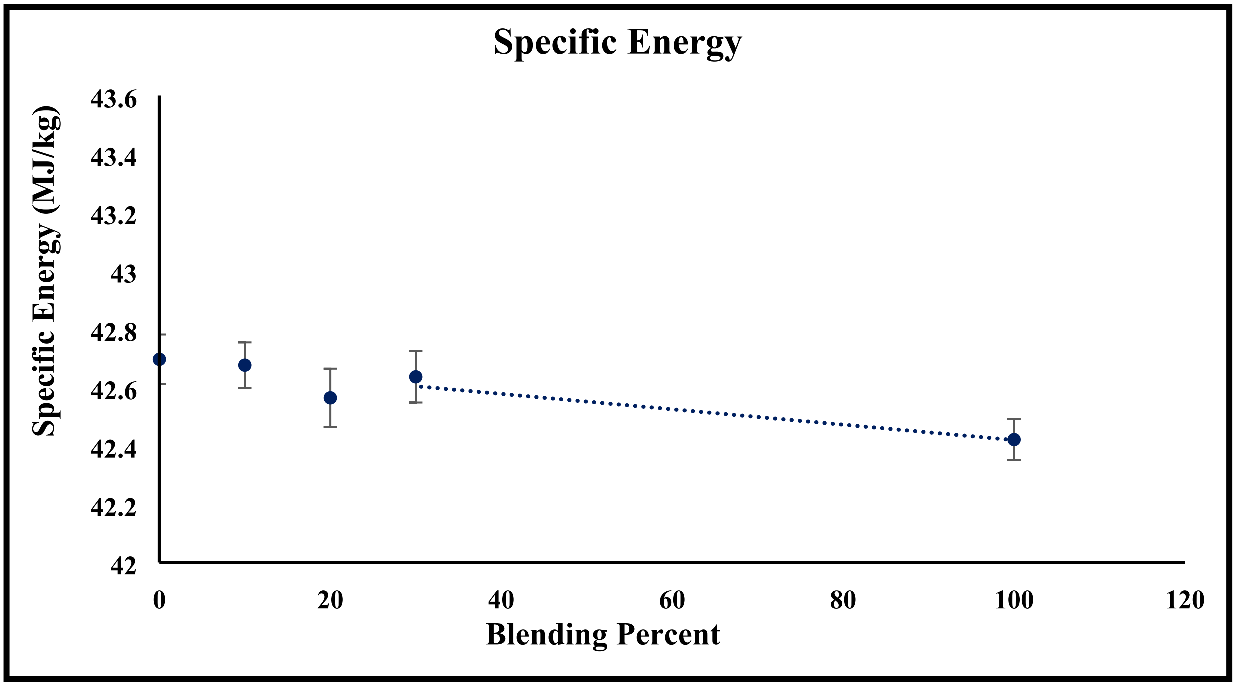
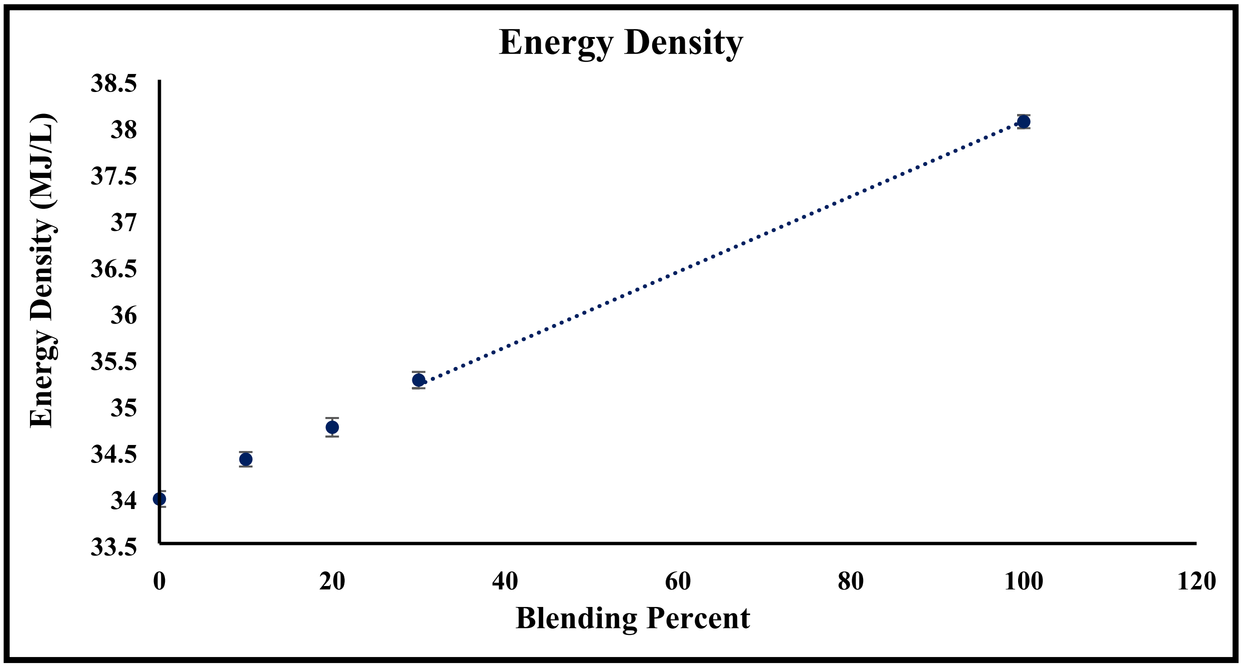


Figure S7. Energy density versus blending percent.



Simulated distillation of 2.

The simulated distillation was completed using a method based on ASTM D2887.[4,5] A standard mixture of ~40 mg/L *n*-octane through icosane in hexane was used to correlate retention time to boiling point.

Figure S8. Simulated distillation curve (boiling point versus retention time).

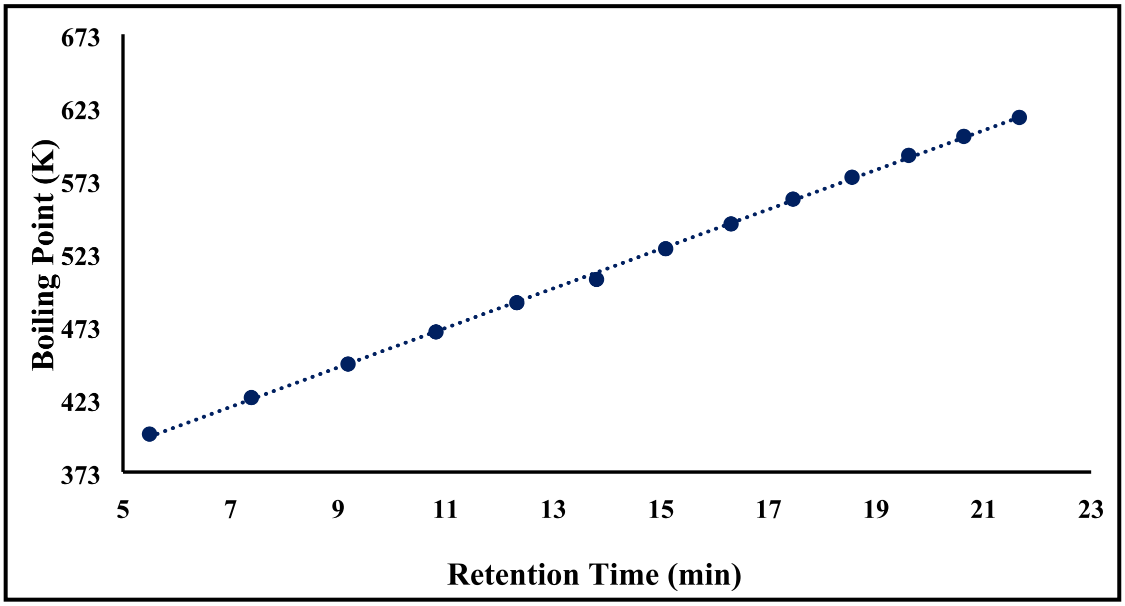


Table S6. Simulated distillation retention time and boiling point data.

	Retention time (min)	Boiling point (K)
C8	5.493	399
C9	7.387	424
C10	9.184	447
C11	10.819	469
C12	12.322	489
C13	13.804	505
C14	15.089	526
C15	16.305	543
C16	17.457	560
C17	18.554	575
C18	19.608	590
C19	20.632	603
C20	21.665	616
2	16.848-18.635	551-575

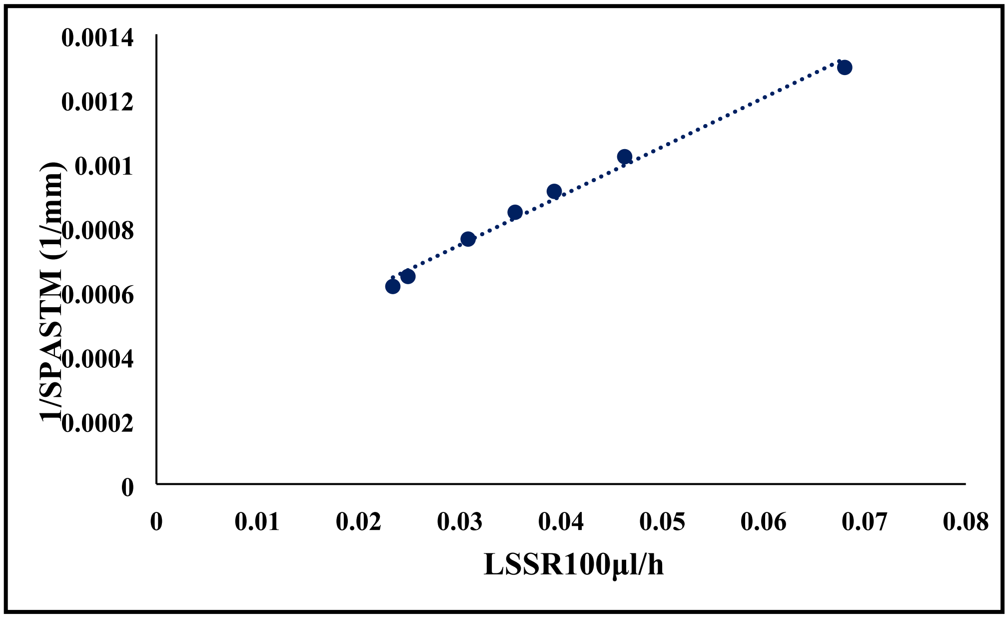
Effective Smoke Point (ESP) Procedure and Data

Sooting tendencies were measured using a variation of the yield-based procedure we developed earlier,[6] and then were converted to effective smoke points (ESPs). The samples were sequentially doped into the fuel of a methane/air nonpremixed flame at a fixed volumetric flowrate of 100 µL/h, and the maximum centerline line-of-sight spectral radiance ($LSSR_{100\mu L/h}$) of each doped-flame at 660 nm was measured. The ESP of each sample was assumed to be inversely related to $LSSR_{100\mu L/h}$:

$$ESP = \frac{C}{LSSR_{100\mu L/h}} + D$$

The constants *C* and *D* were determined by measuring $LSSR_{100\mu L/h}$ for 1-methylnaphthalene and trans-decahydronaphthalene, which have literature smoke points of 5.5 and 22.7 mm.[7] To test the validity of this equation, we measured $LSSR_{100\mu L/h}$ for the seven isooctane/toluene reference mixtures whose smoke points (SP_{ASTM}) are listed in ASTM D1322 for calibrating smoke point lamps.[8] The figure below shows that there is indeed a linear trend between $1/SP_{ASTM}$ and $LSSR_{100\mu L/h}$ for these mixtures.

Figure S9. $1/SP_{ASTM}$ versus $LSSR_{100\mu L/h}$.



The ESP measured for the samples generated in this study are plotted and listed in the figure and table below. As a consistency check, tetrahydronaphthalene was included in the test set, and its measured ESP = 8.5 mm agrees reasonably with the literature value of 7.1 mm.[7]

Figure S10. ESP versus blending percent.

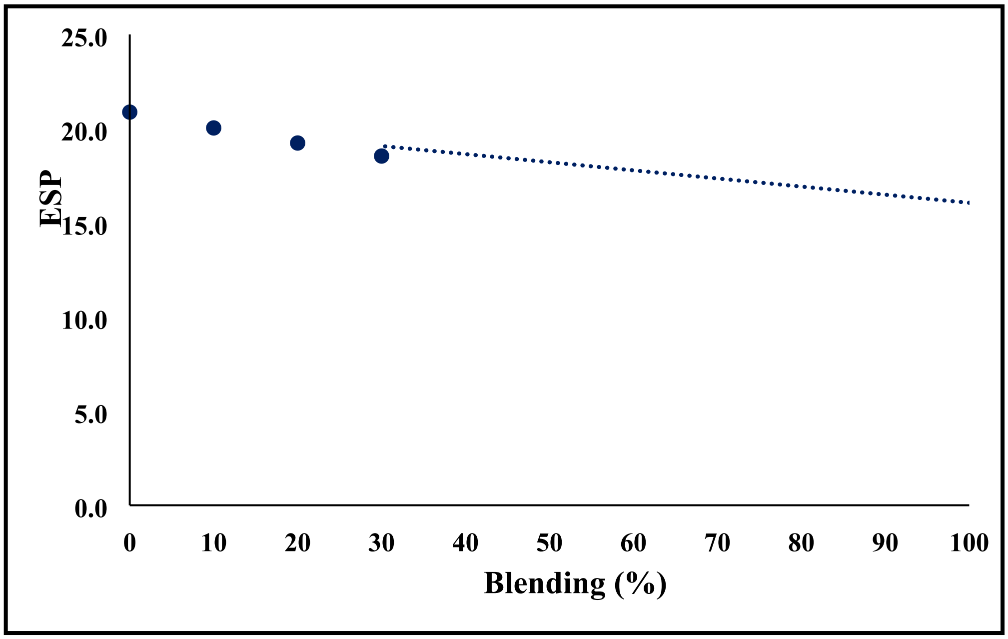


Table S7. ESP data.

Sample	ESP
2	16.3 mm
Jet-A	20.9 mm
10% v/v blend	20.0 mm
20% v/v blend	19.2 mm
30% v/v blend	18.5 mm

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