

Supplemental Information for:

The Sooting Behavior of Lactones as Sustainable Fuels

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SI A. Reactant Abbreviations, Sources, and Purities

The table below lists details of the reactants. The first column lists the common name for each reactant. The second column gives the abbreviation for each reactant used in this study. The abbreviations for the saturated lactones have the general form $N_{C,\text{ring}}-N_{C,\text{total}}-L$, where $N_{C,\text{ring}}$ is the number of carbons in the ring and $N_{C,\text{total}}$ is the total number of carbons. The third column is the source. The fourth column is the purity specified by the vendor. The units for purity are not specified by the vendors, but probably correspond closely to mole percent.

Common Name	Abbreviation	Source	Purity (%)
α -angelicalactone	α -A-L	Thermo Scientific	98
β -propiolactone	3-3-L	Thermo Scientific	97
γ -butyrolactone	4-4-L	Sigma Aldrich	≥ 99
γ -caprolactone	4-6-L	Thermo Scientific	98
γ -heptanolactone	4-7-L	TCI America	98+
γ -undecalactone	4-11-L	Sigma Aldrich	99
γ -valerolactone	4-5-L	TCI America	98+
δ -caprolactone	5-6-L	TCI America	> 99
δ -valerolactone	5-5-L	TCI America	98+
ϵ -caprolactone	6-6-L	TCI America	99+
4-pentenoic acid	4PA	Thermo Scientific	98
5-hexenoic acid	5HA	Thermo Scientific	98
toluene	T	Sigma Aldrich	≥ 99.5
<i>n</i> -heptane	H	Sigma Aldrich	99
isooctane	ISO	Sigma Aldrich	≥ 99
air	n/a	building compressor	n/a
methane	n/a	Airgas	99.99 (“UHP”)
nitrogen	n/a	Airgas	99.999 (“UHP”)

SI B. Schematic Diagram of the Apparatus

The figure below shows the apparatus used in these measurements. SI C gives details of the specific burner. For all flames, the nominal gas-phase flowrate of the oxidizer (air) is 50,000 cm³/min and the nominal gas-phase flowrates of the fuel components are 0.395 cm³/min (test fuel), 282.425 cm³/min (methane), and 112.18 cm³/min (nitrogen). Mass flow controllers (MKS 1559A, Omega FMA5514ST) actively governed the flowrates of the gas-phase components. The controllers for CH₄ and N₂ were directly calibrated for the process gases with a 1000 cm³ bubblemeter. A syringe pump (KDS Scientific 100) controlled the injection rates of the liquid test fuels into the gaseous CH₄/N₂ mixture. SI D lists the liquid-phase flowrates calculated for each test fuel to produce the target gas-phase flowrate, and the property values used in these calculations. Resistive tapes heated all parts of the fuel line to at least 100 °C and the burner to 170 °C. Given this heating, the dopants vaporized rapidly upon injection and were swept to the burner by the other fuel components. A PID controller maintained the burner temperature to within ±1 °C, which was crucial since the soot concentrations in the flame depend sensitively on the initial temperature of the reactants.

The top of the figure shows the apparatus for measuring line-of-sight spectral radiance (L): a UV silica window embedded in the chimney transmits light from the flame to the rest of the setup; a fused silica biconvex lens focuses the light onto a 1 mm diameter circular aperture; an interference filter (Thorlabs FB660-10, frequency width at half maximum = 10 nm, center wavelength = 660 ± 2 nm) and an infrared-blocking filter (Schott KG2) isolate the light at 660 nm; and a red-enhanced photomultiplier tube (PMT; Oriel 77348) detects the light. An A/D converter (LeCroy LT342, 1 MΩ input impedance) samples the PMT output at 5 Hz. Each sample is an average of 50,000 8-bit measures recorded 2 μs apart.

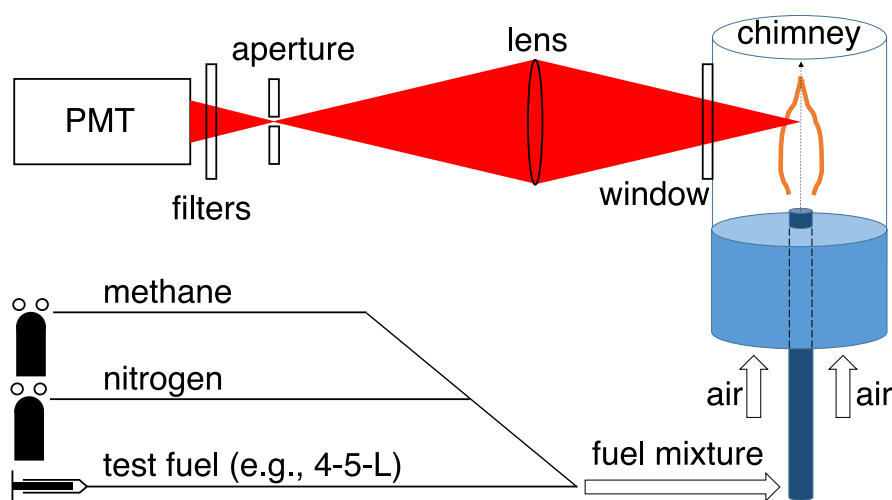


Figure 1. Schematic Diagram of the Apparatus.

SI C. Schematic Diagram of the Burner

The figure below shows details of the burner. All dimensions are given in the original units specified by the suppliers. Reference [1] provides a detailed burner description, including CAD drawings. This burner is being employed by multiple research groups as a standard configuration for experimental and numerical studies of soot formation under the auspices of the International Sooting Flame Workshop [2].

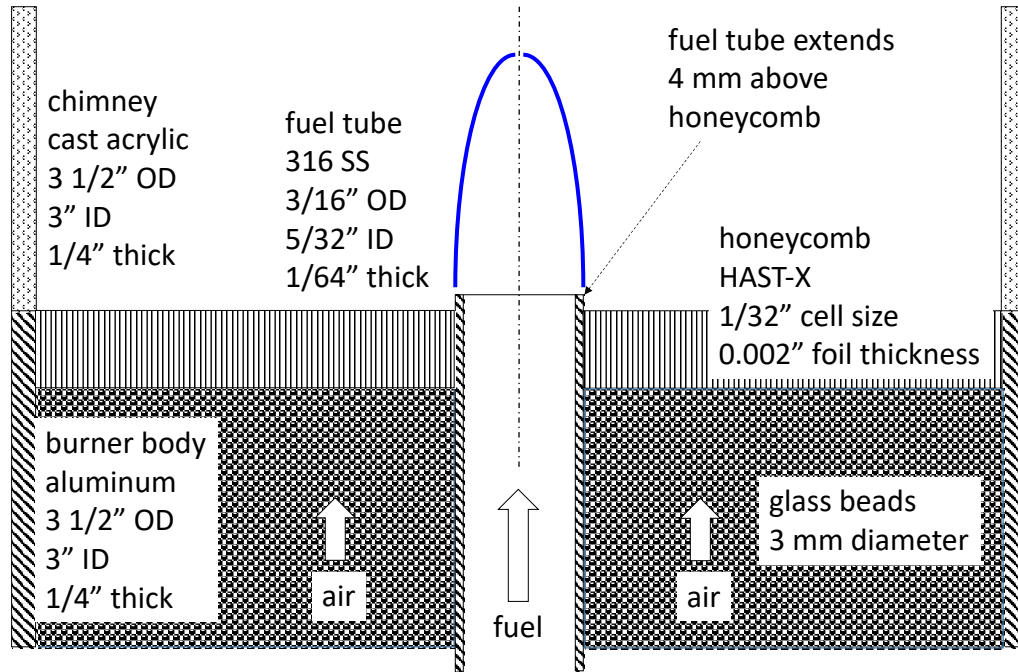


Figure 2. Schematic Diagram of the Burner.

- [1] J. Gau, D. Das, C. McEnally, D. Giassi, N. Kempema, M. Long, Yale Coflow Burner Information and CAD Drawings, (2017) DOI:10.6084/m9.figshare.5005007.v1.
- [2] B. Franzelli, M. Roussillo, P. Scoflaire, J. Bonnetty, R. Jalain, T. Dormieux, et al., Multi-diagnostic soot measurements in a laminar diffusion flame to assess the ISF database consistency, *Proc. Combust. Inst.* 37 (2019) 1355–1363.

SI D. Test Fuel Flowrates

The table below lists the test fuel flowrates used in these measurements. The first column is the abbreviation for each test fuel (see SI A for a key). The second column is the relative molecular mass M_r for each test fuel. The third column is the liquid-phase mass density ρ for each test fuel. The values of ρ for T, H, and ISO are averages of the values from the vendor and [1–3]. These values were measured at a range of temperatures from 20 °C to 25 °C. The values for ρ for all other test fuels were estimated with the group contribution method in [4]. The fourth column is the liquid phase volumetric flowrate Q for each test fuel. These values were input to the syringe pump during the measurements. They were calculated to give a vapor phase volumetric flowrate of 0.395 cm³/min at 296.4 K and 101.7 kPa—typical ambient conditions in our laboratory—using the ideal gas law and the values listed for M_r and ρ . The units and number of significant figures of Q match the required input to the syringe pump.

Test Fuel	M_r (g/mol)	ρ (g/mL)	Q (μ L/h)
α -A-L	98.100	1.090	88.0
3-3-L	72.063	1.105	63.8
4-4-L	86.089	1.072	78.5
4-6-L	114.142	0.998	111.8
4-7-L	128.169	0.979	128.1
4-11-L	n/a	n/a	n/a
4-5-L	100.116	1.024	95.6
5-6-L	114.142	1.021	109.4
5-5-L	100.116	1.061	92.3
6-6-L	114.142	1.059	105.4
4PA	100.116	0.998	98.1
5HA	114.142	0.977	114.3
T	92.138	0.869	103.7
H	100.202	0.686	142.9
ISO	114.229	0.691	161.6

- [1] C.L. Yaws, Yaws' Handbook of Physical Properties for Hydrocarbons and Chemicals, (2008).
- [2] J.R. Rumble, CRC Handbook of Chemistry and Physics, 101st Edition, (2019).
- [3] DIPPR Project 801 - Full Version, Design Institute for Physical Property Research/AIChE, (2019).
- [4] D. Mathieu, R. Bouteloup, Reliable and versatile model for the density of liquids based on additive volume increments, Ind. Eng. Chem. Res. 55 (2016) 12970–12980.

SI E. Equilibration of the Test Fuels with the Fuel Delivery System

The figure below addresses the adsorption of the test fuels onto the walls of the fuel lines and burner. The vertical axis is LSSR signal. The horizontal axis is time t , with $t = 0$ corresponding to starting the syringe pump. The blue line is the instantaneous signal measured for one trial of 4-7-L (γ -heptanolactone). The red line is the steady-state signal, determined by averaging the instantaneous signal from $t = 300$ to 600 s. The instantaneous signal is initially lower than the steady-state value due to net adsorption of 4-7-L onto the initially uncoated walls. However, the signal asymptotes to the steady-state value within about 100 s, which demonstrates that 4-7-L achieves adsorption/desorption equilibrium with the walls on this timescale. The other test fuels have boiling points comparable to or lower than 4-7-L, so they also achieved equilibrium within 100 s. Once this equilibrium is achieved, there is no net loss of the test fuel to the walls, so the test fuel concentration entering the flame is the same as the concentration originally injected into the fuel mixture.

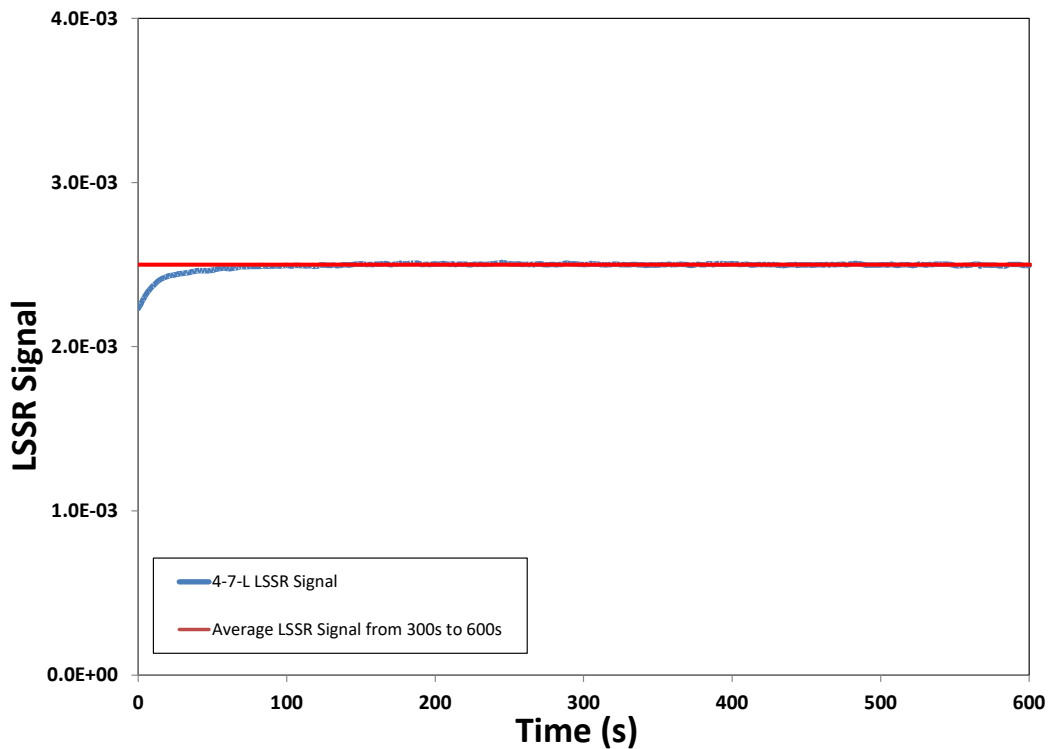


Figure 3. Equilibration of the 4-7-L (γ -heptanolactone).

SI F. Linearity test

The figure below shows the LSSR signal measured for a flame doped with 4-7-L (γ -heptanolactone) as a function of the dopant mole fraction. The data closely fits a linear trend ($R^2 = 0.9969$). This observation demonstrates that all the dopant was evaporating and reaching the flame—if the dopant had been condensing in the fuel lines, then the signal would have flattened out as the dopant concentration exceeded the saturation concentration. The other dopants have boiling points comparable to or lower than 4-7-L, so they would not have condensed either. The linear trend also demonstrates that the LSSR diagnostic was in a linear regime throughout the range of measured signals.

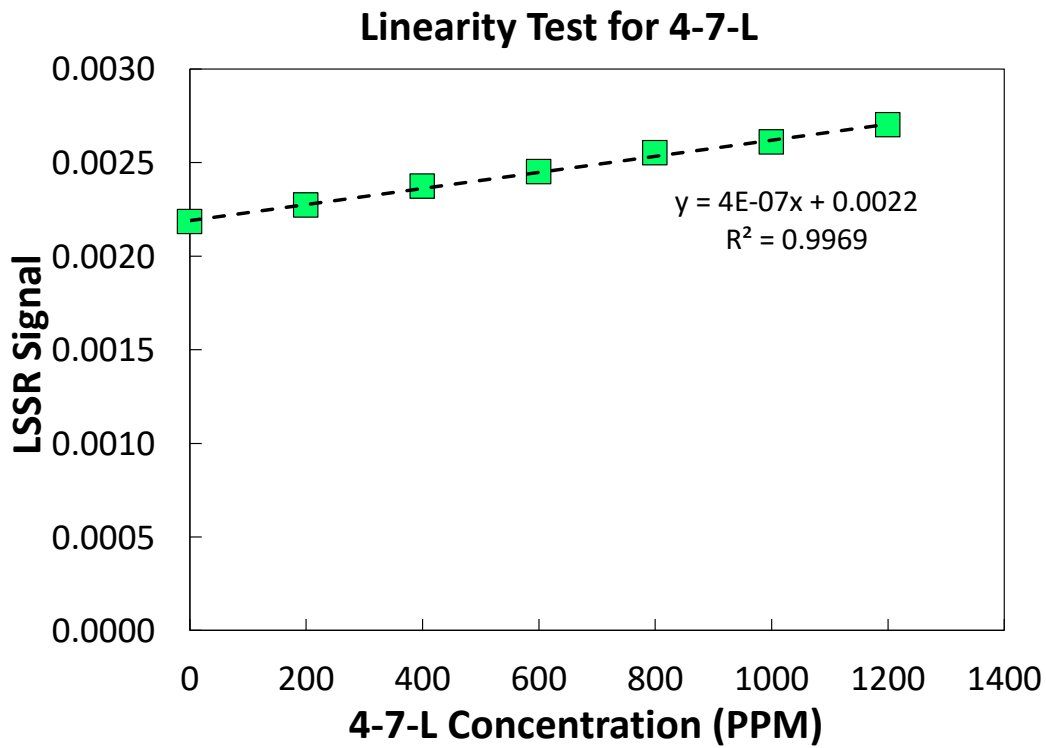


Figure 4. Linearity Test of 4-7-L (γ -heptanolactone).

SI G. YSI Measurements of the Internal Standard

Isooctane was included in every measurement set as an internal standard. The figure below shows its measured YSI as a function of time beginning with the first experiment. It shows that the measured values were consistent over the course of the experiments and agree reasonably with the previously measured value (61.7) [1].

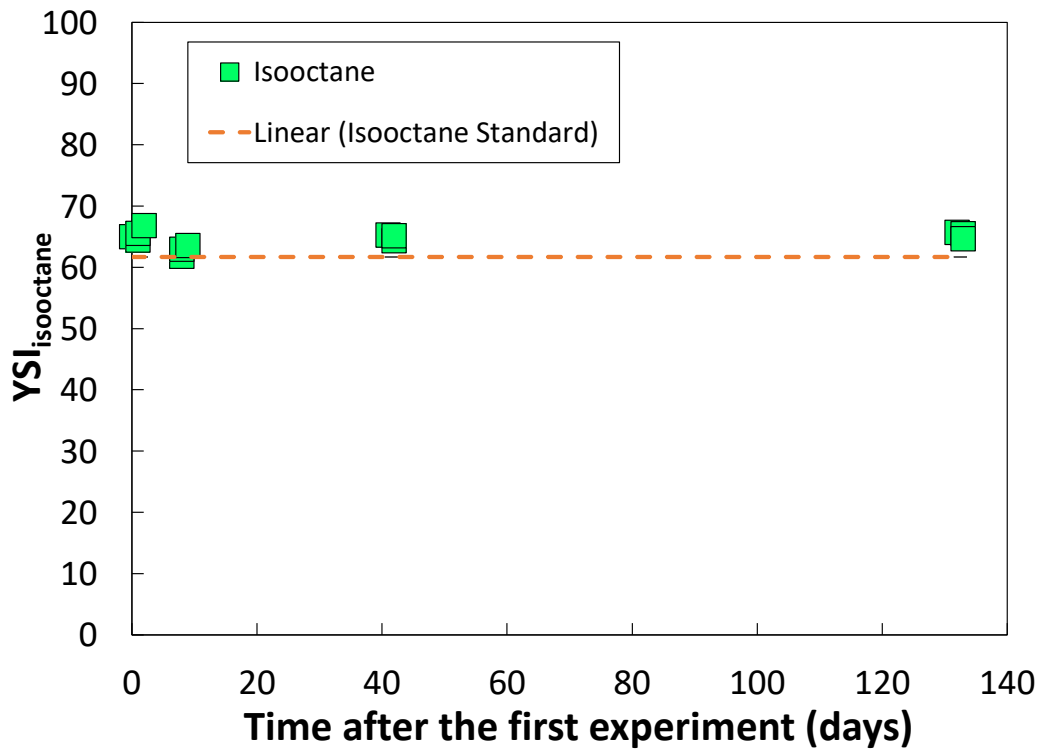


Figure 5. YSI Measurements of the Internal Standard Isooctane.

[1] C.S. McEnally, D.D. Das, L.D. Pfefferle, Yield Sooting Index database volume 2: Sooting tendencies of a wide range of fuel compounds on a unified scale, (2017)
DOI:10.7910/DVN/7HGFT8.

SI H. Data and Sources for Figure 2 of the Main Text

The table below lists the data values and their sources for Figure 2 of the main text. The first column is the designation for each compound or fuel. The pure compounds are test fuels from this study and SI A provides a key to their abbreviations. “Diesel” is a conventional diesel fuel discussed in [6]. “Jet A” is a conventional Jet A fuel discussed in [7]. The “TG” fuels are a set of test gasolines discussed in [3]. These fuels were generated as part of the US Department of Energy’s Co-optimization of Fuels and Engines program. They were produced by conventional fuel refineries and mostly meet the specifications for gasoline, but they were formulated to have enhanced concentrations of alkanes (TG alkylate), aromatics (TG aromatic), alkenes (TG olefin), and cycloalkanes (TG cycloalkane). The E30 is a conventional gasoline blended with 30 vol% ethanol. The second column is the measured value of YSI for each compound or fuel. The third column is the source of the measured YSI value. The fourth column is the lower heating value LHV for each compound or fuel. These values are given as energy/mole since YSI provides a measure of soot/mole. The fifth column is the source of the LHV. For the pure compounds, LHV is calculated with the empirical relation [5]

$$LHV\left(\frac{MJ}{mol}\right) = 0.417 * \left(x + \frac{y}{4} - \frac{z}{2}\right)\#(1)$$

where x , y , and z are the number of C, H, and O atoms in the pure compound. For the pure fuels, measured values of LHV were taken from the cited references. All these references provide values in energy/mass units, so the relative molecular mass M_r of each fuel was required to convert the LHV to energy/mole units. The M_r of the diesel fuel was assumed to match the V2 surrogate defined in [6]. The M_r of the Jet A is the value calculated from a detailed hydrocarbon analysis (DHA) in [7]. The M_r of the TG fuels are values calculated from DHAs in [3].

Name	YSI	YSI Source	LHV (MJ/mol)	LHV Source
<i>Pure Compounds</i>				
3-3-L	8.8	this study	1.2510	Eq. 1
4-4-L	17.2	this study	1.8765	Eq. 1
4-5-L	34.9	this study	2.5020	Eq. 1

4-6-L	41.0	this study	3.1275	Eq. 1
4-7-L	45.2	this study	3.7530	Eq. 1
4-11-L	58.2	this study	6.2550	Eq. 1
5-5-L	21.1	this study	2.7105	Eq. 1
5-6-L	38.0	this study	3.3360	Eq. 1
6-6-L	35.7	this study	3.3360	Eq. 1
α -A-L	18.2	this study	2.2935	Eq. 1
H	36.0	[4]	4.5870	Eq. 1
T	170.9	[4]	3.7530	Eq. 1
<i>Conventional Fuels</i>				
Diesel	256.0	[1]	7.6726	[1]
Jet A	150.0	[2]	6.8413	[7]
TG alkylate	60.9	[3]	4.6383	[3]
TG aromatic	114.9	[3]	3.9955	[3]
TG olefin	81.0	[3]	4.3146	[3]
TG cycloalkane	97.9	[3]	3.7318	[3]
TG E ₃₀	47.9	[3]	2.7421	[3]

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- [1] D.L. Bartholet, M.A. Arellano-Treviño, F.L. Chan, S. Lucas, J. Zhu, P.C.S. John, et al., Property predictions demonstrate that structural diversity can improve the performance of polyoxymethylene ethers as potential bio-based diesel fuels, *Fuel*. 295 (2021) 120509.
- [2] J. Zhu, J.V. Alegre-Requena, P. Cherry, D. Curtis, B.G. Harvey, M.A. Javed, et al., Sooting tendencies of terpenes and hydrogenated terpenes as sustainable transportation biofuels, *Proc. Combust. Inst.* 39 (2023) 877–887.

- [3] C.S. McEnally, Y. Xuan, P. C. S. John, D.D. Das, A. Jain, S. Kim, S, et al., Sooting tendencies of co-optima test gasolines and their surrogates, *Proc. Combust. Inst.* 37 (2019) 961-968.
- [4] C.S. McEnally, D.D. Das, L.D. Pfefferle, Yield Sooting Index database volume 2: Sooting tendencies of a wide range of fuel compounds on a unified scale, (2017).
- [5] K. Schmidt-Rohr, Why combustions are always exothermic, yielding about 418 kJ per mole of O₂, *J. Chem. Educ.* 92 (2015) 2094-2099.
- [6] C.J. Mueller, W.J. Cannella, J.T. Bays, T.J. Bruno, K. DeFabio, H.D. Dettman, et al., Diesel surrogate fuels for engine testing and chemical-kinetic modeling: compositions and properties, *Energy Fuels* 30 (2016) 1445-1461.
- [7] N.A. Huq, G.R. Hafenstine, X. Huo, H. Nguyen, S.M. Tiff, D.R. Conklin, et al., Toward net-zero sustainable aviation fuel with wet waste-derived volatile fatty acids, *Proc. Natl. Acad. of Sci. U. S. A.* 118 (2021) e2023008118.

SI I. Data and Sources for Figure 3 of the Main Text

Bereczky et al. measured particulate matter (PM) emissions for an off-road, four-cylinder, turbocharged, direct injection, water-cooled diesel engine with exhaust gas recirculation [1]. Samples were taken from the exhaust stream before the oxidation catalytic converter and thus represent engine-out PM emissions. Three fuels were considered: (1) a #2 diesel fuel (D), (2) a mixture of the D with a fatty acid methyl ester (FAME) biodiesel (BD), and (3) a mixture of the D and BD with 4-5-L. The D and BD suppliers are only specified as “commercial sources in Hungary”. The BD composition is only specified in terms of the atomic weight percentages, which were C (77%), H (12%), and O (11%). Based on this information, and the typical size range of the molecules in biodiesels, we assume that the BD has the properties of pure methyl linolenate ($C_{19}H_{32}O_2$), which has weight percentages of C (78.1%), H (11.0%), and O (11.0%).

Figure 3 in the main text compares the measured PM mass concentrations in the exhaust for each fuel mixture (Γ_{PM}) with YSI/LHVs we have estimated for each fuel mixture. The following table was used to calculate the values plotted in the figure. The first column is the designation for each fuel mixture used in Reference [1]. The second column is each component j in each fuel mixture. The third column is the mole fraction for each component in each fuel mixture (x_j). The values were calculated in the second table below. The fourth column is the YSI for each component as a pure compound (YSI _{j}). The YSI for D was taken from Bartholet et al. [2]. The YSI for BD was estimated for pure methyl linolenate using the model from SI F. The YSI for 4-5-L was measured in this study (see Table 1 in the main text). The fifth column is the LHV for each component in each fuel mixture (LHV _{j}). The detailed explanation for calculating LHV for D can be found in SI H. The LHV for BD is calculated assuming BD has the properties of pure methyl linolenate ($C_{19}H_{32}O_2$) and using Equation (1) in SI H. LHV for 4-5-L was calculated in the table in SI H. The sixth column is the YSI of each fuel mixture (YSI). The values were calculated with the linear blending rule:

$$YSI = \sum_j x_j * YSI_j$$

where the sum is over all of the components j in the fuel mixture. The seventh column is the LHV of each fuel mixture (LHV). The values were calculated with the linear blending rule:

$$LHV = \sum_j x_j * LHV_j$$

where the sum is over all of the components j in the fuel mixture. The eighth column is the YSI divided by the LHV of each fuel mixture (YSI/LHV). The ninth column is the measured mass concentration of PM in the engine exhaust gases for each fuel mixture (Γ_{PM}). The values were estimated from Figure 18 of Reference [1]. They correspond to the data series for 1900 RPM and full load; we chose these conditions because they produced the largest soot emissions. This data was plotted as a function of the data in the eighth column in the Figure 3 of the Main Text.

Fuel Mixture	Component j	x_j	YSI _{j}	LHV _{j} (MJ/mol)	YSI	LHV (MJ/mol)	YSI/LHV (mol/MJ)	Γ_{PM} (mg/m ³)
100% D					256.0	7.6726	33.3655	124
	D	1.000	256.0	7.6726				
76.9%D + 23.1% BD					240.2	8.1956	29.3086	95
	D	0.835	256.0	7.6726				
	BD	0.165	160.3	10.8420				
71.4%D + 21.5%BD + 7.1% 4-5-L					208.6	7.3200	28.4971	79
	D	0.706	256.0	7.6726				
	BD	0.140	160.3	10.8420				
	4-5-L	0.154	34.9	2.5020				

The following table was used to convert the fuel mixture compositions from the volume fractions specified in Reference [1] to mole fractions. The first and second columns are the same as in the previous table. The third column is the volume fraction for each component in each fuel mixture (φ_j), which were specified in Reference [1]. The fourth column is the relative molecular mass for each component ($M_{r,j}$). The $M_{r,j}$ for D is

the value calculated for the V2 diesel surrogate specified in Mueller et al. [3]. The $M_{r,j}$ for BD is the value for methyl linolenate and was calculated based on its chemical formula ($C_{19}H_{32}O_2$). The $M_{r,j}$ for 4-5-L was calculated based on its chemical formula ($C_5H_8O_2$). The fifth column is the mass density of each component in the liquid phase (ρ_j). The ρ_j for D was the value for the V2 diesel surrogate measured in Mueller et al. [3]. The ρ_j for BD is the value for methyl linolenate estimated with the GCM in [4]. The ρ_j for 4-5-L was estimated with the GCM in [4]. The sixth column is the mole fraction for each component in each fuel mixture (x_j). The values were calculated from the other data in the table. This data was used as input in the table above.

Fuel Mixture	Component j	φ_j	$M_{r,j}$ (g/mol)	ρ_j (g/cm ³)	x_j
100% D	D	1.0	181.2972	0.8466	1.000
76.9%D + 23.1% BD	D	0.769	181.2972	0.8466	0.835
	BD	0.231	292.4562	0.8982	0.165
71.4%D + 21.5%BD + 7.1% 4-5-L	D	0.714	181.2972	0.8466	0.706
	BD	0.215	292.4562	0.8982	0.140
	4-5-L	0.071	100.1158	1.0238	0.154

- [1] Bereczky, K. Lukács, K., M. Farkas, S. Dóbe, Effect of γ -valerolactone blending on engine performance, combustion characteristics and exhaust emissions in a diesel engine, *Natural Resources* 5 (2014) 177–191.
- [2] D.L. Bartholet, M.A. Arellano-Treviño, F.L. Chan, S. Lucas, J. Zhu, P.C.S. John, et al., Property predictions demonstrate that structural diversity can improve the performance of polyoxymethylene ethers as potential bio-based diesel fuels, *Fuel* 295 (2021) 120509.
- [3] C.J. Mueller, W.J. Cannella, J.T. Bays, T.J. Bruno, K. DeFabio, H.D. Dettman, et al., Diesel surrogate fuels for engine testing and chemical-kinetic modeling: compositions and properties, *Energy Fuels* 30 (2) 2016 1445–1461.

[4] D. Mathieu, R. Bouteloup, Reliable and versatile model for the density of liquids based on additive volume increments, *Ind. Eng. Chem. Res.* 55 (2016) 12970–12980.

SI J. YSI predictions

The YSIs of each test fuel were predicted with a group-contribution model (GCM) [1]. The table below lists the results. In this model, the target molecule is decomposed into its component carbon-centered groups (where a group is defined by all the atoms directly bonded to it, the order of the bonds, and whether the central carbon atom is part of a ring), and then its sooting tendency (YSI_{PRED}) is calculated as:

$$YSI_{PRED} = \sum_j C_j * N_j$$

where C_j is the characteristic contribution to YSI from group j , N_j is the number of occurrences of group j in the target molecule, and the sum is over all possible groups. The values of C_j are determined from a training set of molecules with measured YSIs. A tool for making predictions with this model is available online at <https://ysi.ml.nrel.gov/>. This tool recomputes the C_j from its training set each time it makes a prediction. The specific training set at the time of the predictions in the table is included in the SI as a separate file *ysi.csv*. The training set is regularly updated with newly measured values, so the YSIs predicted by it in the future may vary from the values listed in the table.

Abbreviation	SMILES	Predicted YSI
α -A-L	<chem>CC1=CCC(=O)O1</chem>	20.9 ± 17.2
3-3-L	<chem>C1COC1=O</chem>	3.7 ± 17.1
4-4-L	<chem>C1CC(=O)OC1</chem>	11.0 ± 17.1
4-6-L	<chem>CCC1CCC(=O)O1</chem>	25.6 ± 16.8
4-7-L	<chem>CCCC1CCC(=O)O1</chem>	32.2 ± 16.8
4-11-L	<chem>CCCCCCCC1CCC(=O)O1</chem>	58.5 ± 16.8
4-5-L	<chem>CC1CCC(=O)O1</chem>	19.0 ± 16.9
5-6-L	<chem>CC1CCCC(=O)O1</chem>	26.3 ± 16.9
5-5-L	<chem>C1CCOC(=O)C1</chem>	18.4 ± 17.1
6-6-L	<chem>C1CCC(=O)OCC1</chem>	25.7 ± 17.1

4PA	<chem>OC(=O)CCC=C</chem>	32.6 ± 9.2
5HA	<chem>C=CCCCC(=O)O</chem>	39.1 ± 9.2

[1] D.D. Das, P.C. St. John, C.S. McEnally, S. Kim, L.D. Pfefferle, Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale, *Combust. Flame* 190 (2018) 349-364.