SOOTING TENDENCIES OF DIESEL FUELS, JET FUELS, AND THEIR SURROGATES IN DIFFUSION FLAMES

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Abstract

Surrogates of transportation fuels are useful design tools for developing engines with cleaner and more efficient combustion. It is important that information about the sooting tendency of the target fuel be incorporated in the formulation of these surrogates. Toward that end, in this work we report experimentally measured sooting tendencies of several diesel and jet fuels, surrogates of these fuels, and pure compounds which are components of these surrogates. These fuels, surrogates, and compounds were separately doped in trace quantities (0.5% by mass) into the fuel of a methane-air laminar coflow flame. The sooting tendencies, expressed as Yield Sooting Indices (YSIs), were quantified from spatially resolved two-dimensional soot volume fraction distributions of these flames as measured with color ratio pyrometry. Previous means of matching the sooting behavior of the surrogate to the fuel, such as by matching the fuel's hydrogen content or its double bond equivalent, were found to be inadequate because these approaches don't fully account for the effects on the fuel's sooting tendency of branching in aliphatics and *alkyl* substitutions in aromatics. A strong correlation was observed between the YSI and the relative abundance of different types of carbon atoms (as quantified by ¹H and ¹³C NMR spectroscopy) in these fuels and compounds, indicating that such NMR characterization can capture essential structure-specific sooting information of relevance to surrogate formulation. Based on these YSI measurements, we demonstrate two approaches to predict the sooting tendency of a fuel surrogate. These approaches, based on (1) the choice of pure compounds that are blended to create a surrogate, or (2) the distribution of carbon atom types in a surrogate, can be used to tune the surrogate's formulation to match the sooting tendency of its target fuel.

Keywords: YSI; soot volume fractions; diesel surrogate; jet fuel surrogate; NMR fuel characterization

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1. Introduction

Carbonaceous particulate matter emissions from diesel engines, also known as soot, have a significant impact on human health and the global climate. According to the World Health Organization [1], particulate matter (PM_{2.5}) air pollution is a leading cause of mortality worldwide, contributing to over 800,000 premature deaths per year. Human and laboratory studies suggest that soot is a likely carcinogen [2, 3], and exposure to soot poses the greatest risk of cancer of all air pollutants [4]; primary exposure pathways include breathing in air containing soot, either from direct engine exhaust or from its presence in the atmosphere. In addition to harming human health, soot contributes directly to global warming by absorbing sunlight and heating the atmosphere; recent studies indicate that it is the second most important source of climate change, with a radiative forcing only one-third less than CO₂ [5]. Finally, soot also effectively impedes advances in automotive fuel economy because combustion strategies that improve efficiency, such as gasoline direct injection (GDI) and compression ignition (CI; i.e., diesel engines), tend to increase emissions [6]. Fortunately, soot emissions from diesel exhaust have a relatively short persistence in the atmosphere (~1 week [5]), and its anthropogenic nature provides society with a strong control mechanism over its emission. Stakeholders are earnestly pursuing approaches for reducing soot emissions, as the expected benefits would be realized in a foreseeable timeframe [7].

A sustainable approach to realize this reduction is the development and use of a cleaner combustion system. In principle, automotive engineers can use computer simulations to design engines that optimize the tradeoffs between high fuel efficiency and low emissions. However, petroleum-derived fuels, such as diesel, happen to be chemically complex mixtures containing thousands of hydrocarbons [8, 9], which makes computational studies of their fundamental combustion properties intractable. Thus, simplified “surrogate fuels” are useful for representing current transportation fuels [10]. A surrogate fuel is a mixture of a small number of pure compounds whose behavior matches certain characteristics of a target fuel containing many compounds, such as a market diesel fuel. Diesel fuels are an important target fuel for surrogates because diesel engines are a major source of soot emissions [3]. The U.S. military’s adoption of the single fuel forward policy [11] mandates using kerosene-based jet fuels in CI engines in ground vehicles for logistical reasons; aviation fuels such as JP-8 are an additional real-world use case of fuels in CI engines, thereby making them important target fuels for surrogate development. Development of surrogates for these fuels has been an area of active research in the recent past, and several extensive reviews of these efforts are available in the literature. The reader is referred to reviews by Dagaut and Cathonnet [12] and Colket et al. [13] for an overview of work done prior to 2007 to develop jet fuel surrogates, and by Farrell et al. [14] and Pitz and Mueller [10] for an outline on the progress made until 2011 in developing diesel surrogate fuels.

Surrogates are traditionally formulated by mixing components in order to mimic some desired physical and/or chemical properties of the target fuel in a hierarchical fashion. Physical fuel properties of interest frequently include density, viscosity, volatility parameters such as boiling/freezing temperature and distillation curve, surface tension, diffusion coefficient, thermal conductivity, specific heat

capacity, etc. Chemical properties of interest are typically C/H/O content, average molecular weight, heat release rate and total heat release, adiabatic flame temperature, fuel ignition timing and quality, and fuel sooting tendency [15]. Most surrogates in the literature are formulated to match a spectrum of these physical and chemical target fuel properties by matching some measure of the overall chemical composition of the target fuel. Several analytical spectroscopic techniques have emerged recently which provide highly detailed fuel characterization information, allowing researchers to develop surrogates with good compositional fidelity to the target fuel. Such techniques include GC-FIMS (gas chromatography with field ionization mass spectrometry) with PIONA (paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics), GC×GC-FID (two-dimensional gas chromatography with flame ionization detection), and ^1H and ^{13}C NMR (nuclear magnetic resonance) spectroscopy. The gas chromatography techniques quantify mass fractions of each constituent compound as well as different hydrocarbon classes in the fuel. NMR spectroscopy analyses the fuel at the sub-molecular level by classifying the carbon atoms present in the fuel into distinct types based on the nature of the bonds connecting the atoms, and quantifies the mole fraction of each of these types in the fuel. These techniques have been used in the literature to characterize several gasoline [16], jet [17], and diesel fuels [18, 19], as well as guide the development of surrogates for these fuels.

Matching fuel sooting tendency has typically not been a major focus of work on surrogate formulation (and indeed, the sooting behavior of the target fuel was not one of the explicit property targets in [19]). However there are a few works in the literature [20–25] which either explicitly consider the sooting behavior of the target fuel in the formulation of the surrogate, or experimentally compare the sooting behavior of the fuel and its surrogate.

The six-component surrogate developed by Violi et al. [20] (see Table 4 for composition) for a generic JP-8 fuel was one of the first to emulate the sooting tendency, among other physical and chemical properties, of the target fuel. In a related work, Eddings et al. [21] developed a six-component JP-8 surrogate designed to study pool fires. The components (*n*-octane, *n*-dodecane, *n*-hexadecane, xylenes, decalin, and tetralin) were blended in order to match both the boiling point distribution and smoke point of the target fuel. Lemaire et al. [22] developed one of the first surrogates for a commercial low-sulfur diesel fuel which took the sooting tendency of the fuel into account. The diesel fuel and its two surrogates (binary mixtures of *n*-dodecane and 1-methylnaphthalene), were studied in a turbulent diffusion flame; soot loads were quantified with Laser-Induced Incandescence (LII) and Fluorescence (LIF). Sooting tendency was quantified using the Threshold Sooting Index (TSI). One of the two surrogates, which was formulated to match the TSI of the target fuel, produced similar amounts of soot in the flame as the diesel fuel, though differences were observed in the compositions of species on the surfaces of the soot particles collected from the diesel and surrogate flames. Mensch et al. [23] developed surrogates for an aviation fuel, JP-8, by replicating the fuel’s H/C ratio, autoignition characteristics, and sooting tendency. The surrogate was a ternary mixture of two alkanes and a substituted aromatic hydrocarbon (Table 4) chosen to match the TSI of the JP-8 fuel and the surrogate. Dooley et al. [24] also utilized the TSI, along with the average fuel molecular weight, H/C ratio, and

77 derived cetane number, as targets to match a 4-component surrogate to a target Jet-A fuel, POSF
 78 4658. The components of the surrogate (Table 4) were blended in proportions which minimized
 79 the difference between the aforementioned targets for the fuel and surrogate. The performance of
 80 the surrogate was compared to the fuel in several controlled combustion experiments, including
 81 a wick-fed laminar diffusion flame, which was used to measure the smoke points of the fuel and
 82 surrogate. Additionally, soot volume fractions in the flame were quantified using laser extinction;
 83 the peak f_v values were found to be comparable for the fuel and the surrogate at their respective
 84 smoke points. Witkowski et al. [25] studied three real fuels (gasoline, jet fuel, diesel), two alkanes, and
 85 several “simple” surrogate fuels by seeding them in low concentrations (~ 2200 ppm) in a methane/air
 86 nonpremixed flame. The surrogates were binary or ternary mixtures of one or more alkanes (either
 87 *n*-heptane, *iso*-octane, *n*-decane, or *n*-tetradecane) and toluene. Fuel and surrogate sooting tendencies
 88 were quantified from 2D soot f_v maps obtained using laser induced incandescence and laser extinction.
 89 Soot loads were found to match between some target fuels and their surrogates.

90 Most surrogate formulation work involving soot has been for jet fuels and jet fuel applications.
 91 Many of the components utilized in these jet fuel surrogates fall in the front end of the diesel carbon
 92 number range (which is approximately $C_{10} - C_{22}$). Corresponding surrogate literature on diesel fuels
 93 focusing on soot is very sparse [14]. There are several practical reasons for this scarcity. It is typically
 94 difficult to carry out experimental measurements with fuel components of such low volatility in the
 95 diesel boiling range in traditional smoke point apparatus [23]. Experimental apparatuses which rely
 96 on extensive preheating through high-temperature operation to vaporize these fuels risk thermal
 97 degradation of the fuel. Additionally, only a relatively small number of the diesel distillation range
 98 hydrocarbons (e.g., *iso*-paraffins and *cyclo*-paraffins) are available commercially at high purity.

99 To address these concerns, we have developed an experimental approach, utilizing a fuel doping
 100 strategy in a methane/air coflow flame, which allows us to study the sooting behavior of low volatility
 101 fuels and compounds. In this approach, we add small amounts of the fuel or compound of interest
 102 (dopant) to a lightly sooting base flame and measure the resulting increases in soot concentration. The
 103 experimentally measured soot concentrations (expressed as $F_{v,max}$, defined in §3.2 below) are then
 104 converted into apparatus-independent Yield Sooting Indices (YSIs) by the normalization equation:

$$YSI = A \times F_{v,max} + B \quad (1)$$

105 where A and B are apparatus-specific parameters chosen such that the YSI of *n*-hexane = 0, and the
 106 YSI of benzene = 100. The primary advantage of this method is that the additive concentrations - 0.5%
 107 by mass in the fuel - are too small to affect the soot concentrations through indirect mechanisms such
 108 as dilution of the base fuel or changes in the flame temperature; measured sooting tendencies depend
 109 principally on the direct chemical effects of the dopant. Other advantages of this technique include the
 110 small dopant sample volume needed for this technique ($\sim 100\mu\text{L}$), which is two orders of magnitude
 111 lower than the minimum sample volume necessary to measure the smoke point of fuels with the
 112 ASTM-D1322 method [26]. Because 99.5% of the fuel is the same for all the doped flames, soot loads

for all dopants (fuels, surrogates, pure compounds) are measured in identical reactive environments, instead of at the smoke point, which occurs at different flame conditions for different fuels.

The doped flame approach used in this work has been used successfully to experimentally and computationally study the sooting effects of many fuels and pure compounds by our group and others in the literature [25, 27–31]. In a related recent work [32], we demonstrated the feasibility of this approach for studying three high molecular weight/low volatility hydrocarbons which are components of a recent diesel surrogate [19]. In this work, we are extending the experimental approach in [32] to include novel measurements of the YSI of two reference diesel fuels, four reference jet fuels, four diesel surrogates, five jet fuel surrogates, and the components of these surrogates. These fuels and surrogates are listed in Tables 2, 3, and 4. CFA is a certification ultra-low sulfur diesel fuel that is manufactured by Chevron-Phillips Chemical Co. FD9A is a reference diesel fuel developed under the auspices of the Coordinating Research Council [33] to study the effects of fuel-property variations on diesel combustion in engines. POSF 4658 is a composite Jet-A fluid prepared by mixing five individual batches of Jet-A from different U.S. manufacturers. POSF 10264, 10289, 10325 are reference JP-8, Jet-A, and JP-5 fuels respectively, developed under the auspices of the National Jet Fuels Combustion Program [34], and designed to span a range of combustion-related properties, such as flash point, viscosity, and aromatics content. The four diesel surrogates, vOA, vOB, v1, v2, were developed by Mueller et al. [19], and feature increasing levels of compositional accuracy relative to the single target diesel fuel, CFA, upon which they are based. The jet fuel surrogates include formulations featuring 2–6 pure components by Violi et al. [20] (“Sur_1”), Agosta et al. [35], Bruno and Smith [36] (“Modified Aachen”, with 1,3,5-trimethylbenzene substituted for 1,2,4-trimethylbenzene), Mensch et al. [23] (“JP-8 surrogate (22)”), and Dooley et al. [24]. These surrogates were formulated to variously match fuel properties such as volatility, boiling point curves, smoke point, advanced distillation curves, average molecular weight, H/C ratio, derived cetane number, and threshold sooting index. Apart from the “Modified Aachen” surrogate, none of the surrogate formulations have been altered in the preparation of samples for use in this work. The components of these surrogates comprise a set of 25 unique hydrocarbons in total, listed in Table 1.

The objectives of this study are:

1. To demonstrate the feasibility of YSI as a relevant measure of sooting tendency for real fuels and their surrogates, as well as pure compounds.
2. To characterize the sooting tendency (in terms of YSI) for a set of reference diesel and jet fuels, and recently developed fuel surrogates.
3. To generate a consistent set of experimentally determined benchmark YSI data for compounds commonly considered for developing and validating surrogate mixtures for diesel and jet fuels.
4. To develop predictive mixing rules for the YSIs of fuel surrogates based on their chemical compositions.

5. To verify if the sooting behavior of a target fuel can be matched by a surrogate if the surrogate matches the fuel's carbon-type distribution.

2. Experimental methods

The experimental approach and devices used here have been discussed in detail previously [32] and are briefly reiterated here. Atmospheric pressure, axisymmetric, coflowing, nonpremixed, laminar methane/air flames were established on a Yale Coflow burner [39]. Sooting tendencies of pure compounds, diesel and jet fuels, and their surrogates (listed in Tables 1, 2, 3, and 4) were determined by doping them separately into the fuel of a flame and measuring two-dimensional soot volume fraction (f_v) maps using color-ratio pyrometry. The fuel mixture - methane (mass fraction $Y_{CH_4} = 58.3\%$), nitrogen ($Y_{N_2} = 41.2\%$), and a dopant ($Y_{dopant} = 0.5\%$) - flows out of a 4 mm inner diameter tube and reacts with air that flows from the annular region between this tube and an 7.4 cm inner diameter concentric aluminum tube, which acts as a chimney. The nominal reactant flow rates were 282 cm³/min of CH₄, 112 cm³/min of N₂, and 50,000 cm³/min of air. The dopants were added to the fuel on a constant mass-fraction basis in this work (instead of on a constant mole-fraction basis as in previous related works [27, 29, 40]) because, unlike the pure compounds studied earlier, the average molecular weights of the real fuels studied in this work were not known. All dopants were liquids at room temperature, with liquid-phase flowrates ranging from 96 to 146 μ L/hour depending on the liquid-phase mass density. Densities of all diesel and jet fuels and surrogates were measured as part of this work. The measured densities are consistent with values reported in the literature (where available).

Samples of diesel fuels and surrogates were provided by Chevron. Samples of jet fuels were obtained from Wright Patterson Air Force Base. All pure compounds were sourced from Sigma Aldrich. Fuel surrogates in Table 4 were prepared by blending their components volumetrically with Eppendorf Research Plus pipettes (accurate to ± 0.0008 mL); component mass ratios were measured gravimetrically with a Mettler-Toledo XS105DU analytical balance (accurate to ± 0.02 mg). All dopants were dispensed into the gas-phase fuel mixture through a syringe pump (pump = Cole Parmer EW-74900, syringe = Hamilton Gastight 1710). The needle of the syringe charged with the dopant was introduced into the fuel line through a septum in a stainless steel tee. The fuel line and fuel tube were heated to 145°C with temperature-controlled resistive tapes. At these thermal conditions, the vapor pressure [41] of *n*-hexadecane (1110 Pa), which was the least volatile of all dopants used, is approximately 25 times greater than its partial pressure in the fuel mixture (44 Pa). Therefore, all liquid reactants vaporized upon injection and were swept as gases to the flame by other fuel components. Each dopant was allowed to flow for at least 30 min prior to data acquisition. Time-resolved flame luminosity measurements confirmed that all dopants achieved adsorption/desorption equilibrium with the walls of the fuel line and fuel tube within this 30 min interval.

Two-dimensional f_v maps were measured using color-ratio pyrometry. This technique of measuring soot has been used in our previous work [32], and elsewhere in the literature [42–45]. Flames were

Table 1: List of surrogate fuel components and their measured Yield Sooting Index in this study

IUPAC (Common name)	Formula	CAS #	YSI ^d	Structure
benzene ^a	C ₆ H ₆	71-43-2	100	
<i>n</i> -hexane ^a	C ₆ H ₁₄	110-54-3	0	
methylbenzene (toluene)	C ₇ H ₈	108-88-3	172.5	
methylcyclohexane	C ₇ H ₁₄	108-87-2	20.8	
1,3-dimethylbenzene (<i>m</i> -xylene)	C ₈ H ₁₀	108-38-3	193.1	
ethylbenzene	C ₈ H ₁₀	100-41-4	203.4	
2,2,4-trimethylpentane (<i>iso</i> -octane)	C ₈ H ₁₈	540-84-1	23.8	
propylbenzene	C ₉ H ₁₂	103-65-1	181.0	
1,2,4-trimethylbenzene ^b	C ₉ H ₁₂	95-63-6	260.6	
1,3,5-trimethylbenzene (mesitylene)	C ₉ H ₁₂	108-67-8	243.3	
1,2-dihydronaphthalene (dialin)	C ₁₀ H ₁₀	447-53-0	352.1	
1,2,3,4-tetrahydronaphthalene ^b (tetralin)	C ₁₀ H ₁₂	119-64-2	264.4	
decahydronaphthalene (decalin)	C ₁₀ H ₁₈	91-17-8	53.7	
<i>n</i> -butylcyclohexane ^b	C ₁₀ H ₂₀	1678-93-9	17.0	
<i>n</i> -decane	C ₁₀ H ₂₂	124-18-5	7.4	
1-methylnaphthalene	C ₁₁ H ₁₀	90-12-0	471.2	
cyclohexylbenzene	C ₁₂ H ₁₆	827-52-1	224.4	
<i>n</i> -dodecane	C ₁₂ H ₂₆	112-40-3	9.8	
perhydrophenanthrene ^c	C ₁₄ H ₂₄	5743-97-5	76.4	
<i>n</i> -tetradecane	C ₁₄ H ₃₀	629-59-4	9.5	
1,3,5-triisopropylbenzene ^c	C ₁₅ H ₂₄	717-74-8	246.2	
1,3,5-triisopropylcyclohexane ^c	C ₁₅ H ₃₀	34387-60-5	46.0	
<i>n</i> -hexadecane	C ₁₆ H ₃₄	544-76-3	11.7	
2,2,4,4,6,8,8-heptamethylnonane ^b (<i>iso</i> -cetane)	C ₁₆ H ₃₄	4390-04-9	31.0	
2-methylheptadecane ^e	C ₁₇ H ₃₆	1560-89-0	13.5	
<i>n</i> -octadecane ^b	C ₁₈ H ₃₈	593-45-3	15.3	
<i>n</i> -eicosane ^b	C ₂₀ H ₄₂	112-95-8	14.1	

^a YSIs of benzene and *n*-hexane are defined as 100 and 0, respectively^b The YSIs of these compounds were measured in [37]^c The YSIs of these compounds were measured in [32]^d Experimental uncertainty ± 5 YSI units or $\pm 5\%$, whichever is greater^e Predicted using Eq 6

Table 2: Measured YSI for some diesel and jet fuels

	Name	YSI
Diesels [18]	FD9A	111.4
	CFA	122.2
Jet fuels [34]	POSF 4658	75.5
	POSF 10264	49.6
	POSF 10289	86.9
	POSF 10325	70.3

Table 3: CFA diesel surrogate-fuel compositions (mass fractions) from [19] and their measured YSI

Name	Compound	W_i	YSI
VOA	<i>iso</i> -cetane	0.42	89.2
	<i>n</i> -hexadecane	0.32	
	1-methylnaphthalene	0.15	
	decalin	0.11	
VOB	<i>iso</i> -cetane	0.33	121.0
	<i>n</i> -octadecane	0.32	
	tetralin	0.15	
	1-methylnaphthalene	0.12	
	1,2,4-trimethylbenzene	0.08	
V1	<i>iso</i> -cetane	0.35	102.8
	<i>n</i> -octadecane	0.27	
	1-methylnaphthalene	0.11	
	tetralin	0.11	
	1,2,4-trimethylbenzene	0.05	
	decalin	0.04	
	butylcyclohexane	0.04	
	<i>n</i> -hexadecane	0.03	
V2	1,3,5-triisopropylbenzene	0.17	137.1
	<i>n</i> -octadecane	0.15	
	butylcyclohexane	0.15	
	1,3,5-triisopropylcyclohexane	0.13	
	tetralin	0.12	
	1-methylnaphthalene	0.11	
	2-methylheptadecane	0.10	
	perhydrophenanthrene	0.06	
	<i>n</i> -eicosane	0.01	

Table 4: Jet fuel surrogate compositions and their measured YSI

Reference	Compound	W_i	YSI
Bruno & Smith [36]	<i>n</i> -dodecane	0.78	58.0
	1,3,5-trimethylbenzene	0.22	
Mensch et al. [23]	<i>iso</i> -octane	0.49	77.2
	1,3,5-trimethylbenzene	0.27	
	<i>n</i> -dodecane	0.24	
Dooley et al. [24]	<i>n</i> -dodecane	0.50	57.3
	<i>iso</i> -octane	0.24	
	propylbenzene	0.20	
	1,3,5-trimethylbenzene	0.06	
Agosta et al. [35]	<i>iso</i> -cetane	0.35	128.1
	<i>n</i> -dodecane	0.24	
	1-methylnaphthalene	0.22	
	methylcyclohexane	0.13	
	decalin	0.07	
Violi et al. [20, 38]	<i>n</i> -dodecane	0.35	40.8
	tetradecane	0.28	
	methylcyclohexane	0.14	
	<i>m</i> -xylene	0.11	
	<i>iso</i> -octane	0.08	
	tetralin	0.05	

185 imaged at $f/16$ through a Schott BG-7 filter with a 50 mm focal length lens by a Nikon D90 consumer
 186 camera. The D90 utilizes a CMOS sensor ($23.6 \text{ mm} \times 15.8 \text{ mm}$) with 12.2 million pixels (4288×2848)
 187 for an effective spatial resolution of $35 \mu\text{m}$ per pixel in the plane of the flame. The spectral response
 188 of the CMOS sensor in this camera has been fully characterized by Long and coworkers [42]. All
 189 image enhancement options (sharpness, contrast, color, saturation, etc.) were set to either “normal” or
 190 “none”, as applicable. The ISO was set to its lowest value, 200. The image files were saved in the camera’s
 191 .NEF 12-bit lossless compressed raw format, and demosaiced using OMA [46]. Three-dimensional
 192 soot luminosity distributions were tomographically reconstructed from the raw flame images using
 193 the Gaussian basis-set expansion Abel transform method (BASEX) [47]. For each doped flame, 100
 194 images were acquired over a 600 s interval following a 30 min equilibration period. The individual
 195 images were converted into 2D f_v distributions, which were averaged to improve signal/noise and
 196 ameliorate uncertainties associated with dopant flow rate fluctuations. The reconstruction procedure
 197 and all subsequent soot calculations were implemented using in-house Python code, which is available
 198 from the authors upon request.

199 To test our diagnostic procedure, we imaged a series of flames doped with 1-methylnaphthalene
 200 (1MN) at Y_{dopant} ranging from 0.1% to 0.7%. The data in Figure 1 show how the maximum radially
 201 integrated soot volume fraction $F_{v,\text{max}}$ (which is a measure of the total soot load in the flame and is
 202 defined in Eq 2 below) depends on Y_{dopant} . The data closely fit the straight line shown in the figure,
 203 indicating that the measured soot volume fractions in these flames depend linearly on Y_{dopant} at these
 204 doping levels. Additionally, the linear response also indicates that the radiative soot emissions are not
 205 being optically trapped to a significant extent in the flames studied in this work (the sootiest flame
 206 studied in this work is the $Y_{1\text{MN}} = 0.7\%$ flame).

Figure 1: Maximum radially integrated f_v (labeled $F_{v,\text{max}}$) for 1-methylnaphthalene doped flames at different doping levels. The grey line is a least-squares linear fit.

207 3. Results and Discussion

208 3.1. Soot volume fractions

209 In this study, we measured 2D soot volume fraction (f_v) maps for methane flames doped with 27
 210 pure compounds, 6 diesel and jet fuels, and 9 fuel surrogates. Figure 2 shows some representative
 211 results. Hexane and benzene are hydrocarbons used to define the YSI scale (see Eq 1 above), while POSF
 212 4658 and CFA are reference Jet-A and #2 ultra-low sulfur diesel certification fuels, respectively. The
 213 fuel tube ranges from $-2 \leq r \leq 2$ mm in each of the panels in Figure 2, with the coflowing air around
 214 it. The f_v maps were cropped such that height above burner, $z = 0$ mm corresponds to the top edge
 215 of the fuel tube. Because the color ratio pyrometry diagnostic is based on radiative emissions from
 216 flame-heated soot particles, f_v measurements are only available at flame locations with detectable soot
 217 luminosity. Similar f_v maps were obtained for all compounds, fuels, and surrogates listed in Tables 1 –
 218 4 and are available upon request from the authors. All flames were non-smoking, with f_v peaking
 219 at the centerline, and measurable f_v occurring at $z \geq 20$ mm. The doped flames were qualitatively
 220 similar to the undoped flame; however, increased f_v was detected at all locations in all doped flames
 221 compared to the undoped case.

Figure 2: Two-dimensional maps of soot volume fraction in an undoped methane flame (left) and methane flames doped with various test compounds and fuels in Tables 1 and 2. $Y_{\text{dopant}} = 0.5\%$ in all doped flames.

222 3.2. Yield Sooting Index

223 Radially integrated soot volume fractions $F_v(z)$ can be calculated from the full 2D soot maps in
 224 Figure 2.

$$F_v(z) = \frac{1}{\pi R^2} \int_0^R 2\pi r f_v(r, z) dr \quad (2)$$

225 where $R = 6$ mm is the outer edge of the flame image. $F_v(z)$ is an evaluation of the actual soot
 226 load at a given height in the flame [30]. Figure 3 shows $F_v(z)$ for the flames in Figure 2. Using the
 227 maximum value of $F_v(z)$, we can define the dopant's Yield Sooting Index (YSI) using Eq 1 with the
 228 apparatus-specific parameters A and B chosen such that YSI (hexane) $\equiv 0$ and YSI (benzene) $\equiv 100$.
 229 Using the 2D f_v measurements and Eqns 1 and 2, we calculated the YSIs of all compounds, fuels, and
 230 surrogates. YSI measurements for all dopants were repeated at least thrice, with average repeatability
 231 of $\pm 4\%$. The average of the repeated YSI measurements for the dopants are listed in Tables 1 – 4.

Figure 3: Radially integrated soot volume fractions $F_v(z)$ for the flames in Figure 2.

232 3.3. Literature sooting tendency comparisons

233 3.3.1. Threshold Sooting Index

234 Calcote and Manos [48] defined a hydrocarbon's Threshold Sooting Index (TSI) as

$$TSI = a(MW/SP) + b \quad (3)$$

235 based on the compound's molecular weight (MW) and smoke point (SP). The parameters a and b
 236 were used to establish a uniform scale for the TSI and account for smoke point apparatus differences,
 237 analogous to the process used to determine octane and cetane ratings for fuels used in internal
 238 combustion engines. The TSI is significant for being the first numerical scale for sooting tendencies

Figure 4: Threshold sooting indices (TSIs) vs Yield sooting indices (YSIs) for the pure compounds studied in this work, whose TSI values were available from Mensch et al. [23] and Olson et al. [49]. The grey line is a least-squares linear fit.

of pure hydrocarbons which was device independent and inherently determined by a compound's molecular structure. Olson et al. [49] applied this TSI model to smoke point results obtained on the ASTM standard smoke point lamp [26]. They incorporated information from their measurements and from the literature and provided a list of "suggested values" for the TSI of a large range of hydrocarbons. Later, in 2010, Mensch et al. [23] reviewed and collated various literature sooting tendency data sets to assemble a consistent set of TSI values for many potential components of jet fuel surrogates.

Figure 4 shows a plot of the YSIs of the compounds listed in Table 1 vs their TSIs from Olson et al. [49] and Mensch et al. [23] (for compounds listed in both Ref [49] and [23], the value given in the latter is chosen). It can be seen that the YSIs of the compounds measured in this work correlate well with their TSIs reported in [23, 49] over a large sooting range, covering *n*-, *iso*-, and cycloalkanes, and single-, and multi-ring aromatics. **This agreement between the YSI and TSI allows us to draw two conclusions:** (1) Quantifying sooting tendencies based on maximum soot yield in a doped methane/air coflow flame (YSI) is consistent with sooting tendency measurements made with each compound at its own smoke point (TSI). (2) **Because the TSI values of these compounds (derived from smoke point measurements in flames fueled by pure compounds) agree with their YSI values (derived from soot yield measurements in methane flames doped with these compounds), the choice of methane as the base fuel, and its associated chemical implications (such as a preponderance of methyl radicals in the flame), does not confound the sooting tendency measurement.**

257 3.3.2. *Constant mole fraction YSI*

258 McEnally and Pfefferle reported the sooting tendencies of some of the aromatic hydrocarbons in
259 Table 1 in an earlier work [27] in which they introduced the maximum soot yield based YSI approach
260 to measuring sooting tendency. Figure 5 plots the YSIs of the compounds in Table 1 measured in
261 the current work vs their YSIs from [27]. This comparison between the previous measurements,
262 where the compounds were doped into the flame on a constant mole fraction basis, and the current
263 measurements, where the compounds are doped into the flame on a constant mass fraction basis,
264 was done as a sanity check. In general, sooting tendency measurements for aromatics in this work
265 are qualitatively consistent with previous YSI measurements. The actual YSI values from this work
266 and from [27] are expected to disagree for two reasons: (1) The YSI values in [27] were scaled such
267 that benzene $\equiv$ 30 and 1,2,-dihydronaphthalene $\equiv$ 100, whereas in this work, they are scaled to hexane
268 $\equiv$ 0 and benzene $\equiv$ 100. This explains the difference in the relative scale of YSI values between the
269 horizontal and vertical axes in Figure 5. (2) The compounds in [27] were doped into the methane/air
270 flame at a constant *mole* fraction of 400 ppm. In this work, the same compounds were doped at a
271 constant *mass* fraction of 0.5% by weight. Differences in molecular weights and densities between the
272 compounds leads to differences¹ in the actual doping levels of these compounds between this work
273 and [27]. This accounts for deviations from perfect linear agreement (relative spread around the linear
274 trendline) seen in Figure 5.

¹For example, 1,3-dimethylbenzene (13DMB) and 1,3,5-trimethylbenzene (135TMB) are two compounds whose YSI were measured in this work and [27]. 13DMB and 135TMB have very similar densities (0.868 g/ml and 0.864 g/ml respectively); therefore, in this work, they were doped into the flame with similar liquid flow rates. However they have different molecular weights (106.2 g/mol and 120.2 g/mol respectively), and consequently, in [27] the liquid flow rate of 135TMB was approximately 13% greater than 13DMB. These relative differences in doping levels manifest as differences in measured soot yields between this work and [27].

Figure 5: Comparison of yield sooting indices (YSIs) for aromatics doped at constant mole fractions (from McEnally and Pfefferle, 2007 [27]) versus aromatics doped at constant mass fractions (in this work, see Table 1). The grey line is a least-squares linear fit.

3.4. Structural predictions

3.4.1. Hydrogen content

The hydrogen content of a hydrocarbon (either as H/C ratio or H% by weight) is one of the oldest parameters used to predict its sooting tendency [50]. Typically, higher hydrogen content correlates with a greater degree of saturation and a lower tendency to form soot. However, limited predictive capability [48, 51] has been attributed to this parameter, for two major reasons: (1) the tendency to form more soot with decreasing H/C is a weak trend, and (2) a compound's hydrogen content is coupled with its adiabatic flame temperature and therefore the relationship between hydrogen content and sooting tendency could be a manifestation of thermal rather than chemical effects.

Figure 6 shows the relationship between the sooting tendency of a hydrocarbon (quantified by its YSI) and its hydrogen content (H% by mass). The line is drawn as a visual aid. The overall trend suggests sooting tendency increases with decreasing hydrogen content in a hydrocarbon. This is consistent with the observed sooting tendencies of alkanes < cycloalkanes < aromatics in flames and engine studies [52]. However, the single-ring aromatics (▼ in Figure 6) in our dataset do not follow this trend. These aromatics include benzene, and *alkyl*-substituted benzenes, starting with a methyl group (toluene) and ending with tri-isopropylbenzene (TIPB). These *alkyl* substitutions increase the compound's YSI, while also increasing its overall hydrogen mass fraction. Contrary to what would be expected from the increase in hydrogen content, the presence of these non-aromatic substitutions on

293 a benzene ring do not have a dilutive effect on its sooting tendency. Instead, these *alkyl* substitutions
 294 enhance soot formation because they can provide access to additional pathways for aromatic ring
 295 growth [27], which has been shown to be the rate determining step in soot formation in nonpremixed
 296 flames [53].

Figure 6: Comparison of hydrogen content (H% by mass) vs sooting tendency (YSI) for 27 hydrocarbons listed in Table 1.

297 3.4.2. Double Bond Equivalent

298 The double-bond equivalent (DBE) of a hydrocarbon C_nH_m is defined as

$$DBE = 1 + n - m/2 \quad (4)$$

299 It accounts for the level of unsaturation and presence of cyclic ring structures in a hydrocarbon. The
 300 DBE of fuels has been used to represent the effects of fuel molecular structure on their sooting behavior
 301 in the literature. Hanson and Rouvray [54] used the DBE (which they referred to as the hydrogen
 302 deficiency index, HD) in their model to correlate the TSI of hydrocarbon fuels with topological indices.
 303 Aikawa et al. [55] used the DBE in the definition of their empirical particulate matter index (PMI) as a
 304 way to incorporate fuel molecular structure effects on PM emissions from engines.

305 Figure 7 shows the relationship between the DBE and sooting tendency (YSI) of compounds listed
 306 in Table 1. The line, a quadratic fit to the data, is drawn as a visual aid. The overall trend indicates
 307 that sooting tendencies increase with increasing DBE. However, the large range of YSI values for
 308 any given DBE in Figure 7, especially for DBE = 0 and 4, highlights some of the shortcomings of

309 using the DBE as a predictive sooting tendency parameter. DBE does not distinguish between any
 310 alkanes (which all have a DBE of 0, regardless of size or degree of branching). For instance, hexane
 311 and 2,2,4,4,6,8,8-heptamethylnonane (HMN) both have a DBE of 0, but YSI of 0 and 31.0, respectively.
 312 Similarly, DBE does not distinguish between any aromatic compound and any of its *alkyl*-substituted
 313 counterparts. Benzene and 1,3,5-triisopropylbenzene (TIPB) both have a DBE of 4 (the *alkyl* side-chains
 314 in TIPB do not contribute to the DBE), but their YSIs are 100 and 246.2, respectively. These issues rise
 315 primarily from DBE's limited numerical "resolution". DBE can only be integers for pure compounds,
 316 which effectively compresses the fuel structure-specific sooting information into coarse bins.

Figure 7: Comparison of Double Bond Equivalent vs sooting tendency (YSI) for 27 hydrocarbons listed in Table 1.

3.4.3. NMR Carbon-type decomposition

318 ¹³C (carbon) and ¹H (proton) nuclear magnetic resonance (NMR) spectroscopy based techniques
 319 have proven useful in quantifying the compositional characteristics of fuels in the literature [18, 56–60].
 320 These NMR techniques yield fuel composition on a *per-carbon-atom* basis, and can provide better
 321 structure-specific sooting information than “lumped parameters” [61] such as hydrogen content or
 322 DBE, owing to the greater resolution² of the carbon bond types within each molecule. Mueller et al.
 323 [18] used these carbon and proton NMR techniques to quantify the presence of 11 different carbon
 324 types (CT, see Table 5) in two reference diesels and their surrogates.

²For example, *n*-decylbenzene would be characterized as “aromatic” in an analysis based on hydrocarbon-molecule class, but an NMR analysis, as employed by Mueller et al. [18], would show that only 37.5 mol% of the *n*-decylbenzene carbon is

We have developed Multiple Linear Regression (MLR) models to represent the effects of these CTs on the sooting behavior of the compounds listed in Table 1 and in the literature [27, 40]. Similar NMR-based carbon-type MLR models have been developed in the literature to regress various physical (density, viscosity, final boiling point) [60] and chemical (smoke point, aromatics content, heat of combustion, cetane index, octane number) [56, 58, 59, 62] properties of diesels and jet fuels. In the MLR models in this work, the scalar dependent variable is the YSI of the compound, and the explanatory (independent) variables are the number of carbon atoms of each CT in a molecule of the compound.

$$\text{YSI}(\text{predicted}) = \sum_j N_{ij} C_j \quad (5)$$

$$\min \chi^2 = \sum_{i=1}^n [\text{YSI}(\text{expt.}) - \text{YSI}(\text{pred.})]^2 \quad (6)$$

325 N_{ij} is the number of carbon atoms of type j in compound i , and C_j is the specific contribution of
326 CT j . The various C_j are determined by least-squares fitting of Eq 5 to the experimental YSI, which
327 is cast as an optimization problem (Eq 6). This analysis is analogous to the Benson group additivity
328 approach [63] used to estimate the sooting tendency of hydrocarbons [29, 64, 65], with the important
329 distinction being that the “groups” considered here are the aforementioned CTs, whose abundance
330 in real fuels can be quantified experimentally with NMR spectroscopy. Table 5 lists the optimized
331 contributions of each carbon type based on the YSI values of compounds in Table 1.

332 Figure 8 shows the correlation between YSI (predicted) and YSI (experimental) using the optimized
333 values of C_j for three different YSI databases. Figure 8(a) shows the correlation for 26 compounds³
334 whose YSIs were measured in this work and are listed in Table 1; all 11 CTs were represented, with
335 $R^2 = 0.975$. Figure 8(b) shows the correlation ($R^2 = 0.955$) for 52 aromatic hydrocarbons, whose YSIs
336 were measured in [27]. Figure 8(c) shows the correlation ($R^2 = 0.992$) for 45 aliphatic hydrocarbons,
337 whose YSIs were measured in [40]. Because this last database did not feature any aromatic or multicyclic
338 compounds, only 6 CTs (CT1–5, 11) were used in the MLR model.

339 All three datasets satisfied several empirically established criteria regarding size of data set, range
340 of property values, and maximum permissible experimental error [66]. To verify that the goodness
341 of fit observed for these regressions was not due to the presence of too many free parameters (11
342 CTs), we reduced the number of distinct carbon types and developed a “simplified” MLR model for
343 the 45 aliphatic hydrocarbons in the YSI database in [40]. We achieved this reduction by treating
344 secondary (and tertiary) carbon atoms in a linear chain and a ring as the same, i.e., by lumping CT2
345 + CT4 and CT3 + CT5. Figure 8(d) shows the correlation between experimental and predicted YSIs
346 for this simplified model. We see that by ignoring the difference between a carbon atom in a linear
347 chain versus a cyclic ring, the predictive power of the MLR worsens significantly, with the alkanes and

aromatic in character, with the balance having characteristics more representative of alkanes.

³The YSI of 2-methylheptadecane was not measured experimentally and did not feature in the regression.

cycloalkanes clustering into two different groups. This worsening of the fit suggests that the different CTs in Table 5 are necessary to fully describe the compounds’ sooting behavior, and the goodness of fit demonstrated in Fig 8 (a), (b), and (c) is likely not due to overfitting of the data.

Other MLR models developed to predict sooting tendencies in the literature have incorporated topological indices [66], such as the Balaban index [54], the Wiener index [64], the branching index [62], etc. in their regression models. These topological parameters, which quantify the “compactness” of a compound, can provide means to encode the difference between isomers of a compound which differ from each other based on the location of a side chain on the carbon backbone (e.g., 2-methylheptane/3-methylheptane, or *o*-/*m*-/*p*-xylene). We have not observed a significant variation in the sooting tendency between such structural isomers (based on an examination of YSI values of such isomeric cohorts from [27, 40]), and thus have not included such topological indices in the above regression in the interest of model simplicity and ease of use.

The good agreement between the measured and predicted YSIs for all three datasets indicates that the NMR-based CT characterization can capture essential structure-specific sooting information for hydrocarbons of relevance to diesel and jet fuel surrogate formulation.

Table 5: Carbon atom types distinguished by ^{13}C and ^1H NMR-spectroscopy classification technique. Occurrences and C_j are based on the YSIs of compounds in Table 1.

Name	Label	Example	Occurrences	C_j
CH_3	CT1		57	-4.49
<i>n</i> -alkane CH_2	CT2		106	1.52
<i>iso</i> -alkane CH	CT3		9	2.11
cyclo-alkane CH_2	CT4		40	2.71
cyclo-alkane to alkyl-chain CH	CT5		6	19.02
cyclo-alkane to cyclo-alkane CH	CT6		6	13.07
aromatic CH	CT7		58	20.61
aromatic to alkyl-chain C	CT8		16	70.23
aromatic to cyclo-alkane C	CT9		2	85.55
aromatic to aromatic C	CT10		4	112.09
aliphatic C	CT11		4	23.70

3.5. Sooting tendencies of real fuels and surrogates

3.5.1. Smoke points

The smoke point of a fuel is defined in ASTM D1322 [26] as the maximum height of a smokeless laminar diffusion flame of the fuel burned in a wick-fed lamp of specified design. Any increase in fuel flowrate, and consequently the flame height, results in soot escaping from the tip of the flame.

Table 6: Prevalence of carbon atom types in hydrocarbons in three YSI databases. For example, there were 12, 67, and 0 compounds with the CT7 carbon type in this work, M&P 2007 [27], and M&P 2011 [40], respectively.

Carbon type	CT1	CT2	CT3	CT4	CT5	CT6	CT7	CT8	CT9	CT10	CT11
This work	21	13	5	7	4	2	12	9	1	2	2
M&P 2007	55	30	8	7	2	1	67	60	5	14	4
M&P 2011	41	31	19	15	11	0	0	0	0	0	7

Figure 8: Correlation between YSIs of hydrocarbons predicted with Eq 5 using optimized carbon-type contribution values, and measured experimentally (from three different YSI databases). The grey lines in (a), (b), (c), and (d) are the $x = y$ lines, indicating perfect agreement.

Because this onset of soot breakthrough occurs at different flame heights for different fuels, the smoke point has traditionally been considered an important practical predictor of sooting tendency [23]. For instance, the smoke point and parameters based on the smoke point are used to estimate the sooting propensities of jet fuels, with a lower smoke point indicating a greater propensity to form soot.

Figure 9 compares the smoke points of some fuels and surrogates measured in the literature and their YSIs (Tables 2 - 4) measured in this work. Black circles ($\circ$) indicate a reference diesel (CFA) and its surrogates, whose smoke point measurements were reported in [8]. Red triangles (∇) indicate a reference jet fuel (POSF 4658) and its surrogate, whose smoke point measurements were reported in [67]. Blue squares ($\square$) indicate three reference jet fuels, samples and smoke point measurements of which were obtained from Wright Patterson Air Force Base, OH [34, 68]. The dashed lines are drawn as a visual aid. For all three smoke point datasets, decreasing smoke points correlate very well with increasing YSIs. These results, along with the results discussed in §3.3.1, lend credence to the assertion that the doped methane flame strategy of measuring sooting tendency is consistent with pure fuel based flame studies of sooting tendency. There is no evidence that the presence of methane as the base fuel in the flames studied in this work confounds the reported sooting tendency measurements.

Figure 9: Comparison of smoke points vs sooting tendencies (YSI) for diesel, jet fuels, and their surrogates.

3.5.2. Aromatic content

The aromatic content of a fuel is another important practical indicator of its sooting tendency [61]. It is commonly reported as a volume percent as determined by either a fluorescent indicator adsorption test (ASTM D1319 [69]) or a newer supercritical fluid chromatography method (ASTM

387 D5186 [70]). The maximum aromatic content is regulated in many diesels [71] and jet fuels [26]. This
388 has motivated attempts to match the proportion and distribution of aromatics between fuels and their
389 surrogates as a way to ensure fuel surrogates match the sooting behavior of their target fuels.

390 To understand the relationship between fuel aromatic content and sooting tendency, in Figure 10
391 we plot the reported aromatics vol% (via ASTM D1319) for some diesel and jet fuels in the literature
392 [18, 34] vs their YSIs measured in this work (Table 2). The line is a linear best fit line to all data points
393 except the one outlier labeled FD9A.

394 In general, the sooting tendency of all fuels correlates well with their aromatic content as long
395 as their ratio of polyaromatics/monoaromatics is similar. The anomalous behavior of FD9A can be
396 explained by comparing the reported hydrocarbon distributions of the fuels studied here. FD9A (FACE
397 Diesel #9 Batch A) is one of nine Fuels for Advanced Combustion Engines (FACE) reference diesel
398 fuels developed to study the effects of fuel-property variations on diesel combustion in engines [33, 72].
399 Though this fuel was selected for its moderate total aromatics content (one of the three fuel-properties
400 which varied amongst fuels in the FACE project), Mueller et al. [18] noted that the fuel exhibited
401 anomalously high levels of C₈ and C₉ monoaromatics. The other diesel and jet fuels studied in this
402 work showed [18, 34] a more-typical distribution of hydrocarbon class as a function of carbon number.
403 The preponderance of monoaromatics in FD9A would contribute significantly towards the net aromatic
404 fraction of the fuel while contributing incommensurately to its YSI (cf. the difference between the YSI
405 of toluene (monoaromatic, YSI = 172.5) and 1-methylnaphthalene (diaromatic, YSI = 471.2) in Table 1).

406 These findings suggest that while the sooting behavior of a fuel is largely dependent on the
407 aromatics present in the fuel, a lumped parameter such as aromatics volume percent can be inadequate
408 for predicting its sooting tendency. To develop surrogates with fidelity to the sooting behavior of these
409 fuels, it is important to characterize the nature of their aromatic content.

410 3.5.3. *Sooting tendency of real fuel surrogates*

411 In addition to the 27 pure compounds and 6 real fuels listed in Tables 1 and 2, we measured the
412 sooting tendencies of 4 diesel and 5 jet fuel surrogates (see Tables 3 and 4). The measured YSIs of these
413 surrogates agree with established literature sooting tendency information, where available.

414 Mueller et al. [19] reported the smoke points for the CFA diesel and its four surrogates. The YSIs of
415 the fuel and surrogates are consistent with these smoke points (cf. Fig 9); the vOA surrogate has the
416 highest smoke point and lowest YSI (and vice versa for v2). Similarly, Dooley et al. [24] reported in a
417 separate work [73] that their surrogate (TSI = 20.4) had a lower sooting tendency than its target jet fuel,
418 POSF 4658 (TSI = 24.2), which is consistent with the measured YSI values in this work. Finally, Mensch
419 et al. [23] reported that their surrogate matched the TSI of its target JP-8 fuel (TSI = 22) to within
420 experimental uncertainty. Because there is significant variability in the composition of the JP-8 fuel
421 (unlike a reference blend such as POSF 4658), it is difficult to directly compare the YSI of the Mensch
422 surrogate to the jet fuels in this work. However, if we average the YSI of the two JP-8/Jet-A fuels with
423 “normal” properties in Table 2 (POSF 4658 and POSF 10325), we see that the averaged YSI (72.9) agrees
424 with the YSI of the Mensch surrogate (77.2) to within the experimental uncertainty of ± 5 YSI units.

Figure 10: Comparison of aromatic content (in vol%) vs sooting tendencies (YSI) for some diesel and jet fuels. $R^2 = 0.96$.

One of the objectives of this work was to verify if the sooting behavior of a target fuel can be matched by a surrogate if the surrogate matches the fuel's carbon-type distribution. The surrogates developed for the CFA diesel fuel are useful to test this because the four surrogates studied in this work systematically increase in levels of compositional accuracy relative to the target fuel (i.e., the 4-component VOA matches CFA the worst, while the 9-component v2 matches CFA the best). From the YSI values in Table 3, it can be seen that, in general, the similarity in sooting tendency between the surrogates and the fuel increases with increased compositional similarity. The exception to this trend is vOB - it matches the sooting tendency of CFA the best (121 vs 122.2) even though it does not match its composition as well as the v1 or v2 surrogate. We hypothesize that this match is purely coincidental. In general there are many more ways to match the sooting tendency between a fuel and its surrogate without exactly matching the fuel's composition. For example, a binary mixture of 24% (by mass) 1-methylnaphthalene (YSI = 471.2) and 76% *n*-hexadecane (YSI = 11.7), as per YSI mixing rule (Eq 7a) in the following section, can be synthesized to match the YSI of CFA exactly, while not matching the carbon type distributions of the fuel (this binary mixture would have no cycloalkane-type carbon atoms, while ~30% of the carbon atoms in CFA belong to this category [18]). Another example of this phenomenon is the HEX-12 surrogate developed by Eddings et al. [21], which matched the sooting tendency of its target (JP-8) fuel despite having very different carbon atom distributions, as determined through NMR measurements (see Table 2 in [17]). The results of this section and §3.4.3 lend support to the hypothesis that developing surrogates for a fuel by matching the fuel's carbon-type distribution is sufficient but not necessary to match the fuel's sooting behavior.

445 3.6. *Mixing rules to predict YSI*

Based on the measured YSIs of these pure compounds, and the YSI contributions from the different carbon types in §3.4.3, we can predict the YSI of the surrogates in two ways,

$$\text{YSI}_{\text{SM}} = \sum_{i=1}^M W_i \times \text{YSI}_{\text{PC}} \quad (7a)$$

$$\text{YSI}_{\text{SM}} = \sum_{i=1}^M W_i \times \left(\sum_{j=1}^{11} N_j \times C_j \right)_i \quad (7b)$$

446 where YSI_{SM} is the predicted YSI of the surrogate mixture, W_i is the mass fraction of compound i in
 447 each surrogate (listed in Tables 3 and 4), YSI_{PC} is the measured YSI of the pure compound (listed in
 448 Table 1), M is the number of compounds in each surrogate, N_j is the number of carbon atoms of type
 449 j in compound i , and C_j is the contribution of each carbon type to the YSI (Table 5).

450 Figures 11 and 12 show comparisons between the experimentally measured YSIs of the fuel surro-
 451 gates in Tables 3 and 4 (“Measured”) and their predicted YSIs based on the component mixing rule
 452 (Eq 7a, “Predicted - A”) and carbon-type mixing rule (Eq 7b, “Predicted - B”). It can be seen that we
 453 can accurately predict the sooting tendency of the surrogates using either the measured YSI of their
 454 constituent compounds (4% average error of prediction) or the YSI contributions from the various
 455 carbon atom types present in the surrogate (5% average error of prediction). This has two major
 456 implications. First, the YSIs of the pure compounds in Table 1 can be used as design parameters in the
 457 development of new fuel surrogates, as the sooting tendency of a surrogate composed of a mixture
 458 of these compounds can be predicted accurately using Eq 7a. Second, the relative accuracy of the
 459 predicted YSIs using the carbon-type mixing rule (Eq 7b) makes it possible to expand the surrogate
 460 palette beyond the compounds listed in Table 1. For instance, the YSI of one of the components of
 461 diesel surrogate v2, 2-methylheptadecane, was not measured in this work. Although this precluded
 462 using Eq 7a to predict the YSI of v2, all carbon atoms in 2-methylheptadecane were of either type CT1,
 463 CT2, or CT3. Therefore, we could predict the YSI of the v2 surrogate using Eq 7b to be 134 ± 15 , which
 464 compares very favorably to its measured YSI of 137.1 ± 5 .

Figure 11: Comparison of measured and predicted sooting tendencies of some diesel surrogates.

Figure 12: Comparison of measured and predicted sooting tendencies of some jet fuel surrogates.

465 4. Conclusion

466 In this work, we demonstrate the suitability of the doped-flame experimental method for comparing
 467 sooting tendencies of surrogates and their target diesel and jet fuels. We report these sooting tendencies
 468 in terms of yield sooting indices (YSIs) for 2 diesel fuels, 4 jet fuels, 4 diesel fuel surrogates, 5 jet fuel
 469 surrogates, and 25 pure hydrocarbon compounds which are components of these surrogates. These

YSIs are derived from full two-dimensional soot volume fraction maps for methane/air flames doped with these fuels and compounds. We observe a strong correlation between the sooting tendency and the relative abundance of different types of carbon atoms present in these fuels and compounds. We also demonstrate two approaches to predicting the YSI of a fuel surrogate, which can be used to tune the surrogate's formulation to match the sooting tendency of a target fuel. These results present the opportunity for developing new surrogates, composed of hydrocarbons with well-studied chemistry, which can be used to replicate the sooting behavior of most fuels.

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