Two-dimensional soot volume fraction measurements in flames doped with large hydrocarbons

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Abstract

Developing diesel surrogates that mimic the essential characteristics of target fuels such as their sooting tendency and volatility is a necessary but challenging endeavor, owing in part to the scarcity of available experimental sooting data for compounds in the appropriate high molecular weight range. To address this, in this work we demonstrate an experimental approach which provides quantitative sooting data for such compounds. Specifically, we have measured spatially resolved two-dimensional soot volume fraction distributions for three large hydrocarbons: 1,3,5-triisopropylbenzene (TIPB), 1,3,5-triisopropylcyclohexane (TIPCX), and perhydrophenanthrene (PHP), as well as benzene and *n*-hexane. Measurements were performed in methane/air coflowing flames whose fuel was doped separately with these compounds (dopant mass fraction 0.5%). Color-ratio pyrometry was used to measure soot temperature and soot volume fraction distributions. Sooting tendencies were TIPB > benzene > PHP > TIPCX > hexane. These data are expected to be useful in formulation of surrogates with greater fidelity to the volatility and sooting characteristics of real diesel, and in validation of numerical soot models involving such surrogates.

Keywords: diesel surrogates, color-ratio pyrometry, YSI

1. Introduction

Particulate matter emissions from diesel engines are a major source of soot in the atmosphere today, accounting for about 70% of emissions in Europe, North America, and

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Latin America [1]. Soot has been identified as the second most important individual climate-warming agent after carbon dioxide [1]. Exposure to elevated levels of airborne particulate matter, of which soot forms a major portion, has been identified as one of the most important risk factors in reducing global human life expectancy [2]. In response, regulations for vehicular particulate matter emissions are expected to increase in stringency in the future. Developing new transportation engines that meet current (and future) emissions regulations and increasing fuel efficiency standards is one of the major challenges in combustion today. A promising research avenue to address this challenge is the *co-optimization* of next-generation engines and fuels [3]. Unfortunately, the large parameter space involved in engine technology, fuel composition, and combustion strategy makes simultaneous optimization through traditional build-and-test methodologies impractical, leaving computational tools as the most cost- and time-efficient alternative design process [4].

Formidable challenges remain in coupling engine-relevant computational fluid dynamics with detailed chemical kinetics of real fuels. Petroleum-derived fuels are complex mixtures of thousands of chemical components, making detailed numerical combustion simulations involving such fuels unfeasible into the foreseeable future. A practical alternative in numerical simulations is the use of surrogate fuels, which are mixtures of a limited number of pure compounds whose behavior matches certain chemical and physical characteristics of a target fuel (such as a market diesel fuel). Much work has been done on developing and characterizing surrogates for diesel [5].

One of the challenges identified in [5] is the need for candidate surrogate fuels to mimic essential characteristics of the target fuel such as its volatility and sooting tendency. Any surrogate palette, defined as a set of pure compounds that can be blended together to create a surrogate fuel [4], aiming to reproduce such properties of the target fuel *must* include high molecular weight *n*-, *iso*-, and cyclo-alkanes (mol. wt > 140), as well as aromatics in the C₈-C₂₂ range, frequently with one or more side-chains or ring substitutions. For instance, surrogates developed in [4] to match various properties of two real-world diesel fuels included nine different *n*-alkanes, *iso*-alkanes, mono- and dicycloalkanes, mono- and diaromatics, and a naphtho-aromatic. The choice of surrogate compounds included in the palette was constrained by, among other factors, the relative scarcity of experimental combustion data available for hydrocarbons in this size and volatility range. There are a number of reasons for

44 this scarcity. Hydrocarbons in the aforementioned classes typically have very low volatility,
45 making it difficult to study them in the gas phase in combustion experiments. Aromatics and
46 naphtho-aromatics in general have high sooting tendency [6], which makes flames fueled
47 purely by these compounds sooty and consequently problematic for typical diagnostics.
48 Additionally, from a purely practical standpoint, many of these large compounds are not
49 available commercially, or in large quantities, and must be purified or synthesized from crude
50 sources at a significant cost.

51 Nonetheless, there is need for experimental data for such compounds in order to facilitate
52 both the development of new fuel surrogates, and provide validation data for computational
53 models of these surrogates. As a motivating example, Mueller et al. [4] noted substituted
54 monoaromatic and cyclo-alkanes with greater molecular weights than the compounds they
55 included in their surrogate palette to be better representatives of the constituent hydrocarbon
56 classes in their target fuels. Their initial surrogate palette did not include such compounds
57 owing to their lack of availability and relevant experimental data for one or more of the
58 reasons noted above. To address the lack-of-data issue, in this work we demonstrate an
59 experimental approach that makes it possible to study such compounds and provide experi-
60 mental data relevant to the development of surrogate fuels and validation of their numerical
61 combustion models. Specifically, we have measured two-dimensional soot volume frac-
62 tions and temperature in a methane/air nonpremixed coflow flame whose fuel was doped
63 separately with 1,3,5-triisopropylbenzene (TIPB), 1,3,5-triisopropylcyclohexane (TIPCX), and
64 perhydrophenanthrene (PHP) (Figure 1). TIPB and TIPCX are *iso*-alkane substituted aromatic
65 and cyclic-alkane compounds, while PHP is a fully saturated 3-ring hydrocarbon. This exper-
66 imental data provides a more complete and quantitative insight into the sooting behavior
67 of these compounds, which cannot otherwise be obtained from general sooting propensity
68 rankings of the hydrocarbon classes that these compounds belong to (i.e., aliphatic < cyclic
69 < aromatic). In a very recent work, Mueller et al. [7] prepared surrogates with TIPB, TIPCX
70 and PHP as they are in the requisite size and volatility range and have *iso*- and cyclo-alkane
71 nature more characteristic of the compounds found in commercial diesel fuel. To the best of
72 the authors' knowledge, apart from PHP (threshold sooting index reported in [8]), this work
73 is the first reported experimental sooting measurement of these compounds in the literature.

Figure 1: Test compounds studied in this work.

74 The experiments in this work were conducted on methane/air coflow flames generated
 75 with a slightly modified Yale Coflow burner. Previous work [9] on ethylene flames using
 76 this burner have been identified as target flames for computations (*Coflow 3*) at the Second
 77 International Sooting Flame Workshop held in 2014 [10]. The doped flame approach used
 78 in this work has been used successfully to experimentally and computationally study the
 79 structure-specific sooting effects of several large hydrocarbons by our group and others in
 80 the literature [6, 11–15]. Using doped flames to study these test compounds also provides
 81 the added benefit of requiring very small quantities ($\leq 100 \mu\text{l}$) to conduct experiments.
 82 Modifications to the Yale Coflow burner in the current work include provisions for heating
 83 the fuel tube, which is necessary to maintain the test compounds in the gas phase. The
 84 diagnostic used to measure soot volume fractions and temperature is color ratio pyrometry.
 85 This technique has been used to study soot in N_2 -diluted ethylene flames in the literature
 86 [16], and the results have been used to validate computational soot models [17].

Table 1: Dopant physical properties and flow parameters

Compound	Formula	Mol. Wt	Purity	B.P. ^a (°C)	ρ^b (g/ml)	Flow ^c ($\mu\text{l/hr}$)	YSI ^d
1,3,5-triisopropylbenzene	$\text{C}_{15}\text{H}_{24}$	204.35	$\geq 95\%$	234	0.867	111.1	237.3
1,3,5-triisopropylcyclohexane	$\text{C}_{15}\text{H}_{30}$	210.4	$\geq 98\%$	255	0.858	112.3	42.4
perhydrophenanthrene	$\text{C}_{14}\text{H}_{24}$	192.3	$\geq 98\%$	279	0.949	101.5	71.2
<i>n</i> -hexane	C_6H_{14}	86.18	$\geq 99\%$	68	0.661	145.8	0 ^e
benzene	C_6H_6	78.11	$\geq 99.9\%$	80	0.883	109.1	100 ^e

^a Sources: TIPCX – prediction from www.chemspider.com, PHP – experimental from Ref. [18], others – Sigma Aldrich

^b (For all dopants except *n*-hexane) Measured in this work at 21.7 °C, uncertainty $\pm 1.2\%$, *n*-hexane – Sigma Aldrich

^c Liquid phase flowrate dispensed with syringe pump

^d Yield sooting index (YSI). Measured for TIPB, TIPCX, and PHP in this work, uncertainty $\pm 5\%$

^e YSI of *n*-hexane and benzene defined as 0 and 100 respectively

87 2. Experimental

88 2.1. Burner and flame details

89 The experimental setup in this work is similar to that in [16]. Atmospheric pressure,
 90 overventilated, axisymmetric, coflowing, nonpremixed laminar flames were generated with a

91 Yale Coflow burner in which fuel flows from a 0.4 cm inner diameter vertical stainless steel
 92 tube, and oxidizer flows from the annular region between this tube and a 7.4 cm inner diameter
 93 concentric aluminum tube. This outer tube acts as a chimney and isolates the flame from the
 94 lab environment. The fuel tube was open, while the annular oxidizer-flow region contained a
 95 nickel-alloy (HastelloyTM-X) honeycomb. Similar burners (without the outer chimney) have
 96 been used in previous experiments by our group and others at Yale University and elsewhere
 97 [9, 10, 16, 19]. The oxidizer was air, while the fuel was a mixture containing methane (mass
 98 fraction $Y_{\text{CH}_4} = 58.3\%$), nitrogen ($Y_{\text{N}_2} = 41.2\%$), and a test compound ($Y_{\text{dopant}} = 0.5\%$).
 99 The nominal reactant flow rates were 286 cm³/min of CH₄, 115 cm³/min of N₂, and 50,000
 100 cm³/min of air. All gas flowrates were governed by electronic mass flow controllers (calibrated
 101 with soap bubble meters). Benzene, *n*-hexane, and TIPB were catalog items, while TIPCX
 102 and PHP were custom synthesized by Sigma Aldrich. The dopants were liquids at room
 103 temperature, with liquid-phase flowrates ranging from 101.5 to 145.8 $\mu\text{L}/\text{hour}$. The dopant
 104 flowrates varied because they have varying liquid-phase mass densities. Density data for two
 105 of the dopants (TIPCX and PHP) was not available in the literature; therefore densities of these
 106 compounds and TIPB were measured as a part of this work and are listed in Table 1. The test
 107 compounds were dispensed into the gas-phase methane/nitrogen fuel mixture through a
 108 syringe pump (pump = Cole Parmer EW-74900, rate of travel accurate to $\pm 0.25\%$; syringe
 109 = Hamilton Gastight 1710, syringe diameter specified to $\pm 1\%$ of its nominal value by the
 110 manufacturer). The liquid flow rates contained an oscillation (average amplitude about mean
 111 value $\sim 10\%$ or less) whose period matched the period of the pump leadscrew (36 seconds
 112 for PHP, less for other dopants); thus flames were imaged over a 600-s interval to include
 113 several full periods of the oscillation. The needle of the syringe charged with the dopant was
 114 introduced into the fuel line through a septum in a stainless steel tee. The fuel line and fuel
 115 tube were heated to 145 °C with temperature-controlled resistive tapes. At these thermal
 116 conditions, the vapor pressure [18] of PHP (which was the least volatile of all dopants used) is
 117 approximately 30 times greater than its partial pressure in the fuel mixture (11.3 Torr vs. 0.38
 118 Torr). Thus all of the liquid reactants vaporized upon injection and were swept as gases to
 119 the flame by the other fuel components. Each test compound was allowed to flow for at least
 120 30 min prior to data acquisition. Time-resolved flame luminosity measurements confirmed

121 that all test compounds achieved adsorption/desorption equilibrium with the walls of the
122 fuel line and fuel tube within this 30 min interval.

123 2.2. Color ratio pyrometry

124 Soot temperatures and volume fractions (f_v) were measured using color-ratio pyrometry
125 [16, 20–22]. This technique utilizes imaging radiative emissions from soot heated to high
126 temperatures ($\sim 1500 - 2000\text{K}$) in a flame, combined with soot emissivity and Planck's law,
127 to infer soot temperature, and subsequently, soot volume fractions.

128 For this work, the technique used in [16] was followed. Flames were imaged at $f/16$
129 through a Schott BG-7 filter with a 50 mm focal length lens by a Nikon D90 consumer
130 camera. The spectral response of this camera has been fully characterized by Long and
131 coworkers [16]. The D90 utilizes a CMOS sensor ($23.6\text{ mm} \times 15.8\text{ mm}$) with 12.2 million
132 pixels (4288×2848) for an effective spatial resolution of $35\text{ }\mu\text{m}$ per pixel in the plane of the
133 flame. All image enhancement options, such as sharpness, contrast, color, and saturation
134 were set to either “normal” or “none”, as applicable. The ISO was set to its lowest value, 200.
135 The image files were saved in the camera's .NEF 12-bit lossless compressed raw format, and
136 demosaiced using OMA [23].

137 Soot emissivity (ϵ_{soot}) and dimensionless extinction coefficients (K_{ext}) were assumed
138 to be $\lambda^{-1.38}$ and 8.6 respectively as per [16, 24]. Color ratio pyrometry measurements of f_v
139 with these values of ϵ_{soot} and K_{ext} have been shown to agree well with other conventional
140 techniques for measuring f_v such as LII in the literature. A flame-heated, glowing Type-
141 S thermocouple (Pt/Pt-10%Rh) was used as the calibrated light source as per [20]. The
142 emissivity of the thermocouple in the 400 to 700 nm wavelength range was calculated from a
143 second order polynomial fit to the measured emissivity as reported in [20]. The performance
144 of the optical system was validated in two ways. First, the glowing Type-S thermocouple was
145 imaged at several temperatures between $1300 - 1900\text{K}$. Excellent agreement was observed
146 between the self-reported thermocouple temperatures and temperatures determined through
147 color-ratio pyrometry. Second, color-ratio pyrometry measurements for two of the N_2 -diluted
148 ethylene/air flames in [16] (40% and 60% flames) were replicated in the current experimental
149 setup. The measured soot temperatures and f_v for these flames were found to agree very
150 well with the results reported in [16] as well as with LII measurements in the same flames as
151 reported in [25]. This indicated that the optical system had been characterized accurately.

152 2.3. Radial profile reconstruction

153 In color-ratio pyrometry, the captured flame images are two-dimensional line-of-sight
154 projections of the three-dimensional soot luminosity distribution in the flame. To extract
155 soot temperatures and f_v , it is necessary to first tomographically reconstruct this distribution
156 from the 2D projection. Since the coflow flames studied here are axially symmetric, we
157 employ the Gaussian basis-set expansion Abel transform method (BASEX) developed by
158 Dribinski et al. [26] to perform the reconstruction. This method and its derivatives are
159 the most popular reconstruction technique in the fields of photofragment-ion spectroscopy
160 [27]. In contrast to other common reconstruction techniques, this method avoids using
161 the inverse Abel transform, which is noted for being numerically impractical owing to
162 singularities in its definition and needing estimates of derivatives of noisy experimental data.
163 The BASEX reconstruction technique is also fast and computationally inexpensive since it
164 relies primarily on matrix multiplication. To the best of the authors' knowledge, this is the
165 first implementation of this technique for analyzing flame images. Additional details about
166 this method are available in [26, 28, 29]. The reconstruction procedure and all subsequent
167 temperature and soot calculations were implemented using in-house Python code, which is
168 available from the authors upon request.

169 3. Results and discussion

170 3.1. Soot volume fractions

171 Figure 2 shows two-dimensional f_v maps for a series of methane/air coflow flames doped
172 with the test compounds in Table 1. The fuel tube (not pictured) extends from $|r| \leq 2$ mm,
173 with the coflowing air around it. The flame images were cropped such that height above
174 burner, $z = 0$ mm corresponds to the top edge of the fuel tube. Since the color ratio pyrometry
175 diagnostic uses radiative emissions from flame-heated soot particles, temperature (and f_v)
176 measurements are available at only those flame locations with detectable soot luminosity.

177 The doped flames are qualitatively similar to the undoped flame. For all flames, peak f_v
178 occurs along the flame centerline and measurable f_v occurs at $z \geq 20$ mm. The peak f_v (and
179 total soot loading) is greatest for the aromatic compounds (with TIPB > benzene), followed
180 by the cyclic compounds (PHP > TIPCX), with hexane producing the least soot of all dopants
181 tested. Increased f_v was detected at all locations in all doped flames compared to the undoped

case, demonstrating that the diagnostic is capable of discerning changes to the base flame caused by addition of the dopants in concentrations as low as 0.5% by mass.

Figure 3 shows two-dimensional temperature maps for a series of methane/air coflow flames doped with the test compounds in Table 1. The soot temperatures are very similar for the undoped and doped flames; the average temperature varies by less than 50 K across these flames. This observation is consistent with previous thermocouple measurements of temperatures in undoped and doped flames [30]. Nonetheless, soot temperatures seem to decrease with increasing soot levels. Figure 4 shows the average soot temperatures of the six flames plotted against the maximum radially integrated f_v (defined below in Sec 3.2) in those flames. A clear inverse correlation between soot temperature and soot loading in these flames is evident. In contrast, the adiabatic flame temperature is basically unchanged between the various flames (2185.3 K for undoped, 2185.9 K for the doped flames), indicating that the overall thermal conditions in all flames is similar. Therefore, the most likely explanation for the observed changes in the soot temperature is that while both undoped and doped flames have similar *gas* temperatures, increased f_v in the doped flames lead to greater radiative heat losses from the soot particles, and therefore lower measured *soot* temperatures. Changes in the f_v in these flames are caused by chemical effects due to the dopants, and not by their thermal effects.

3.2. Yield sooting index (YSI)

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

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

Figure 5 shows $F_v(z)$ for the undoped and doped flames. $F_v(z)$ is an evaluation of the actual soot load at a given height in the flame [14]. Using the maximum value of $F_v(z)$, we can define the doped compound's Yield Sooting Index (YSI) as per Eq (2)

$$\text{YSI} = A \times |F_v|_{\max} + B \quad (2)$$

where A and B are chosen such that the YSI of benzene and hexane are 100 and 0, respectively. Table 1 lists the YSI of TIPB, PHP, and TIPCX measured with this approach. It is worth noting that, owing to the ease of tailoring exposure times of the camera, and thus utilizing its

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

Figure 3: Two-dimensional maps of soot temperature in an undoped methane flame (left) and methane flames doped with various test compounds. $Y_{\text{dopant}} = 0.5\%$ in all doped flames.

Figure 4: Relationship between average soot temperature and soot loading, represented as maximum radially integrated f_v or $F_v(z)$, for undoped and doped flames.

Figure 5: Radially integrated soot volume fractions $F_v(z)$ for undoped and test compound-doped flames.

209 full dynamic range, this diagnostic allows YSI measurements of compounds whose sooting
 210 tendency spans a wide range.

211 3.3. Linearity

212 To identify the response of the diagnostic to changes in Y_{dopant} , we imaged a series of
 213 flames doped with TIPB at Y_{dopant} ranging from 0.1% to 0.7%. The data in Figure 6 show how
 214 $|F_v(z)|_{\text{max}}$, defined in Eq (1), for these flames depends on their Y_{dopant} . The data closely fit the
 215 straight line shown in the figure, indicating that the measured soot volume fractions in these
 216 flames depends linearly on Y_{dopant} at these doping levels. Therefore, soot emissions are not
 217 being optically trapped to a significant extent in the flames studied in this work. Additionally,
 218 this linear response allows for the amelioration of uncertainties associated with dopant flow
 219 oscillations (as noted in Section 2.1) by imaging the flame, converting each individual image

Figure 6: Maximum radially integrated f_v for TIPB-doped flames at different doping levels. $R^2 = 0.999$ for linear fit.

into a 2D soot distribution, and averaging these distributions over several full periods of oscillations.

3.4. Stochastic variations in radial inversion

Tomographic reconstruction of the 3D soot luminosity distribution from a line-of-sight 2D projection is a mildly ill-posed problem [31], and typically produces noisy reconstructions along the centerline. This leads to significant uncertainty in the measured f_v in the $|r| \leq 1$ mm region of the flame. To quantify this uncertainty, we collected a sequence of 1000 images for an undoped flame (286 cm³/min of CH₄, 115 cm³/min of N₂, $Y_{\text{dopant}} = 0$). Figure 7 shows a comparison of variations in the measured luminosity and the corresponding f_v for this set of images at two heights. While the raw luminosity profiles are essentially identical (max $\sigma \leq 2\%$), the measured f_v profiles have a $\pm 2\sigma$ window spanning as much as 0.02 ppm ($\sim 30 - 50\%$) near the centerline. We attribute these variations to asymmetries in measured luminosity profiles and amplification of experimental noise in the tomographic reconstruction process. We are currently investigating implementing regularization techniques [31], which are expected to help reduce this uncertainty, especially along the centerline.

3.5. Soot luminosity as a validation parameter

The ultimate goal of these soot measurements is to validate numerical soot models. Towards that aim, Connelly et al. [17] have demonstrated a new approach to comparing results from experiments and numerical simulations. Exploiting recent advances in detailed numerical soot models, which provide more complete information about f_v within simulations, they derived predictions of directly measured soot luminosity (“computed signals”) and

Figure 7: Comparison between (line-of-sight) luminosity and (radially-inverted) f_v profiles at two heights. Solid line is average of 1000 images, shaded region represents 95% ($\pm 2\sigma$) confidence interval.

241 compared it to experimental soot luminosity images. Such comparisons of soot luminosity
 242 were found to yield quantitative information similar to that obtainable through the more
 243 traditional (experimental f_v vs. simulated f_v) comparison. We note that there are two major
 244 advantages in the computed signals approach of soot model validation. First, comparing soot
 245 luminosity profiles allows us to avoid the signal degradation inherent in the tomographic
 246 reconstructions necessary to derive f_v from soot luminosity. Second, understanding soot
 247 inception and growth processes, and their effects on soot morphology, is one of the most
 248 active areas of research today, and is expected to further our understanding of the relationship
 249 between soot age and its optical properties. This future knowledge can be incorporated into
 250 numerical soot models, making comparisons with experimental luminosity data tenable,
 251 since “true” information about soot structure, morphology, and optical properties are already
 252 encoded into these luminosity measurements, in contrast to the reported f_v , which are biased
 253 by our assumptions about these properties.

254 4. Conclusion

255 In this work, we report novel measurements of full 2D soot volume fraction and tempera-
256 ture maps and yield sooting indices (YSI) for three compounds: 1,3,5-triisopropylbenzene
257 (TIPB), 1,3,5-triisopropylcyclohexane (TIPCX), and perhydrophenanthrene (PHP). Measure-
258 ments were conducted on methane/air flames whose fuel was separately doped with these
259 compounds, using color-ratio pyrometry as the diagnostic. TIPB was the most sooting com-
260 pound (YSI = 237.3), followed by PHP (YSI = 71.2) and TIPCX (YSI = 42.2) on a scale where
261 benzene and *n*-hexane have YSI of 100 and 0 respectively. We have demonstrated the feasibil-
262 ity of using color-ratio pyrometry on doped flames to measure quantitative full-field f_v for
263 such high molecular weight, low-volatility compounds while using very low sample volumes
264 ($\leq 100 \mu\text{l}$). The large dynamic range of the diagnostic also allows quantitative soot measure-
265 ments for compounds over a significant range of sooting tendencies. This work is expected
266 to be of relevance in formulating new diesel surrogates, and validating computational soot
267 models involving such compounds.

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