

AN IMPROVED METHOD OF SMOKE POINT NORMALIZATION

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The most widely used method of normalizing laminar smoke points from different studies has been the threshold sooting index (TSI). TSI has several drawbacks, particularly a nonphysical dependence on fuel molar mass. An improved normalization method, called normalized smoke point (NSP), is introduced here. For each fuel, NSP is a weighted average of the smoke point lengths measured by different studies. NSP eliminates the major TSI drawbacks. NSP values were determined for 112 hydrocarbons by averaging 256 smoke point measurements from 12 past studies. This allows for the most extensive evaluation to date of the effects of fuel type on the smoke points of hydrocarbon diffusion flames. Hydrocarbon sooting propensity generally increases with increasing fuel carbon/hydrogen atom ratio. For n-alkanes, sooting propensity increases with carbon number, however it generally decreases with carbon number for alkenes and 1-alkynes. Sooting propensity generally increases according to alkanes < alkenes < 1-alkynes < aromatics.

Keywords: Flame length; Laminar diffusion flame; Soot; Sooting propensity; TSI

INTRODUCTION

A smoke point is the condition (and the luminous length) of a laminar diffusion flame that does not emit soot, but that would transition to sooting if the fuel flow rate were increased by any amount. This transition is a result of increased residence time and increased ratio of soot formation/oxidation time (Dotson et al., 2011; Glassman, 1989; Lautenberger et al., 2005; Sunderland et al., 1994). Smoke points have been measured for over 100 gaseous and liquid fuels, and even for a few solids.

Smoke points are the prevailing measure of fuel sooting propensity in laminar diffusion flames, with reduced sooting propensities indicated by increased smoke points. Smoke points also correlate with sooting behavior of turbulent flames, including soot volume fractions, radiative emissions, smoke emissions, and fire behavior (Beji et al., 2008, 2011; Lautenberger et al., 2005; Lemaire et al., 2010). Smoke

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points are increasingly used as fuel sooting properties in computational models of flames and fires (Beji et al., 2008, 2011; Chatterjee et al., 2011; Lautenberger et al., 2005).

Several smoke point normalizations have been introduced (Calcote and Manos, 1983; Kewley and Jackson, 1927; Minchin, 1931) to yield a quantity that, unlike smoke point, increases with sooting propensity. Normalizations also have been used to account for variability in measured smoke points, which arises because smoke points depend weakly on the burner or wick diameter, whether a wick is used for liquid fuels, the coflow velocity (Berry Yelverton and Roberts, 2008; Dotson et al., 2011), the burner velocity profile (Berry Yelverton and Roberts, 2008), and the method of soot emission detection.

Calcote and Manos (1983) introduced the most widely used normalization, called the threshold sooting index (TSI), but its continued wide use may be problematic, as discussed below. Although TSI has been used to correlate the sooting propensities of fuel/fuel mixtures (Gill and Olson, 1984; Mensch et al., 2010; Yan et al., 2005; Yang et al., 2007), identical correlations can be obtained using smoke point lengths (Li and Sunderland, 2011).

An alternative measure of fuel sooting propensity in diffusion flames is yield sooting indices (YSI), which have been reported for several hundred fuels (McEnally and Pfefferle, 2007, 2009, 2011). Test fuels are doped into a methane diffusion flame, and the peak soot volume fraction is measured. This requires little fuel and is precise even for highly sooty fuels. However, it may not fully capture the sooting behavior at higher fuel concentrations.

In this article, an improved method of smoke point normalization—the normalized smoke point (NSP)—is introduced. Published smoke points (in air at 1.0 bar) are used here to determine NSP for 112 hydrocarbons. Effects of fuel type, carbon/hydrogen atom ratio (C/H), and carbon number are examined.

HYDROCARBON SMOKE POINTS

As summarized in Table 1, hydrocarbon smoke points from 12 studies are considered here: Studies 1–6, which were considered by Calcote and Manos (1983), and Studies 7–12, which are more recent. These are all the known studies that report smoke points of at least six pure hydrocarbons burning axisymmetrically in air at 1.0 bar. These studies contain 256 smoke point measurements of 112 hydrocarbons.

Among the 12 studies, seven burned liquid hydrocarbons supplied with wicks (Gill and Olson, 1984; Gülder, 1989; Hunt, 1953; Mensch et al., 2010; Minchin, 1931; Olson et al., 1985; Schalla and McDonald, 1953). As shown in Table 1, wick diameters for these studies vary from 4.4–6.4 mm, and such variation does affect smoke point length (Allan et al., 2009). Clarke et al. (1946) and Van Treuren (1978) used wickless burners with fuel supplied to conical pools. Others supplied pre-vaporized fuel to round burner tubes with air coflow (Ladommatos et al., 1996) or without it (Schalla and McDonald, 1953; Tewarson, 1986). Gaseous hydrocarbons from three studies are considered here: Schug et al. (1980) used forced air coflow, while Schalla and McDonald (1953) and Tewarson (1986) used chimneys.

While 11 of these 12 studies reported smoke point lengths, Schalla and McDonald (1953) reported only smoke point fuel flow rates. These measurements

Table 1 Studies considered, burner or wick diameters, d , number of hydrocarbon smoke point measurements, N , and optimized fitting constants A

Study	Reference	d , mm	N	A
1	Minchin, 1931	4.4	6	1.475
2	Clarke et al., 1946	<64	25	0.880
3	Hunt, 1953	6.4	72	0.873
4	Schalla and McDonald, 1953	4.7, 9	38	0.994
5	Van Treuren, 1978	11.3–62.2	7	0.920
6	Schug et al., 1980	10	8	0.991
7	Gill et al., 1984	5.5	10	1.025
8	Olson et al., 1985	5.6	42	1.175
9	Tewarson, 1986	9	8	1.125
10	Gülde, 1989	4.7	10	0.870
11	Ladommatos et al., 1996	10	16	1.235
12	Mensch et al., 2010	5.5	14	0.965

were converted here to approximate smoke point lengths for hydrocarbons using

$$L_{SP} = c \dot{m}_{SP} \quad (1)$$

where L is luminous flame length, SP is smoke point, c is a constant for all hydrocarbons burning in air at 1.0 bar, and \dot{m} is fuel mass flow rate. Equation (1) is predicted by the Roper (1977) theory when two parameters are constant for all hydrocarbons: smoke point length divided by stoichiometric length and air/fuel volume ratio divided by fuel molar mass. The proportionality between flame length (both stoichiometric and luminous) and fuel mass flow rate for various hydrocarbons is also supported by measurements (Olson et al., 1985; Sunderland et al., 1999; Urban et al., 2000). A fit to the 42 hydrocarbon smoke point measurements of Olson et al. (1985) yields $c = 24.2 \text{ m-s/g}$ and a coefficient of determination of $R^2 = 0.997$. This value of c is used in Equation (1) to estimate the smoke point lengths of Schalla and McDonald (1953).

The smoke points of many oxygenated hydrocarbons have been measured (Allan et al., 2009; Clarke et al., 1946; Ladommatos et al., 1996; Minchin, 1931; Tewarson, 1986; Van Treuren, 1978). Because only a few of these were measured by more than one study, oxygenated hydrocarbons are not considered below.

TSI NORMALIZATION

Combustion research has a long history of attempting to account for the *decreased* sooting propensities that are associated with *increased* smoke points. Kewley and Jackson (1927) defined sooting propensity as

$$S = 32 \text{ mm} - L_{SP} \quad (2)$$

which Minchin (1931) modified to

$$S = (320 \text{ mm})/L_{SP} \quad (3)$$

Neither definition was adopted by others, but they did motivate Calcote and Manos (1983) to introduce TSI, which has been used widely (e.g., Barrientos and Boehman, 2010; Eddings et al., 2005; Gill and Olson, 1984; Lemaire et al., 2009, 2010; Mensch et al., 2010; Olson et al., 1985; Pepiot-Desjardins et al., 2008; Yan et al., 2005; Yang et al., 2007).

Calcote and Manos (1983) defined sooting propensity as

$$S \propto MW_{fuel}/L_{SP} \quad (4)$$

where \propto denotes proportionality and MW is molar mass. Like Kewley and Jackson (1927) and Minchin (1931), they neither justified the chosen functional dependence between S and L_{SP} nor related S to any sooting behavior other than smoke points. Combining Equations (1) and (4) yields

$$S \propto 1/Q_{fuel, SP} \quad (5)$$

where Q is the volumetric flow rate. Calcote and Manos (1983) erroneously included MW_{fuel} in the numerator of their version of Equation (5), introducing ambiguity in their definition of TSI and errors in their analyses of data from Schalla and McDonald (1953) and Schug et al. (1980). They expressed Equation (4) as

$$TSI = a MW_{fuel}/L_{SP} + b \quad (6)$$

where a and b are fitting constants unique to each study.

The TSI normalization has significant drawbacks, as follows:

1. The inclusion of MW_{fuel} in Equations (4) and (6) is problematic. Consider, for example, the two n -alkanes n -C₉H₂₀ and n -C₁₆H₃₄, both having smoke points near 110 mm (Clarke et al., 1946; Olson et al., 1985; Schalla and McDonald, 1953). Two diffusion flames burning these fuels at matched fuel mass flow rates (and thus at nearly matched flame lengths, heat release rates, and stoichiometric air flow rates) will exhibit similar sooting behavior. However, Equation (4) attributes a sooting propensity to n -C₁₆H₃₄ that is 77% higher than that of the lighter fuel, which is impossible for fuels of matched smoke points.
2. TSI is proportional to neither L_{SP} nor its reciprocal; see Equation (6). This can be especially problematic for fuels with long smoke points.
3. TSI varies from 0–100 for most fuels, which is arbitrary, and some fuels have negative TSI (Calcote and Manos, 1983; Olson et al., 1985), which is not physical and is problematic in computational models.
4. Two fitting constants are used, whereas one is shown below to be sufficient.
5. The order in which the normalization is performed affects the values of a , b , and TSI. For example, changing this order can change TSI for 1,3-butadiene from 9.23 to 25.

Calcote and Manos (1983) considered six experimental studies of hydrocarbon smoke points and obtained fitting constants a and b for these. Their empirical success is evaluated here using Figure 1. For each fuel considered, this plots the arithmetic

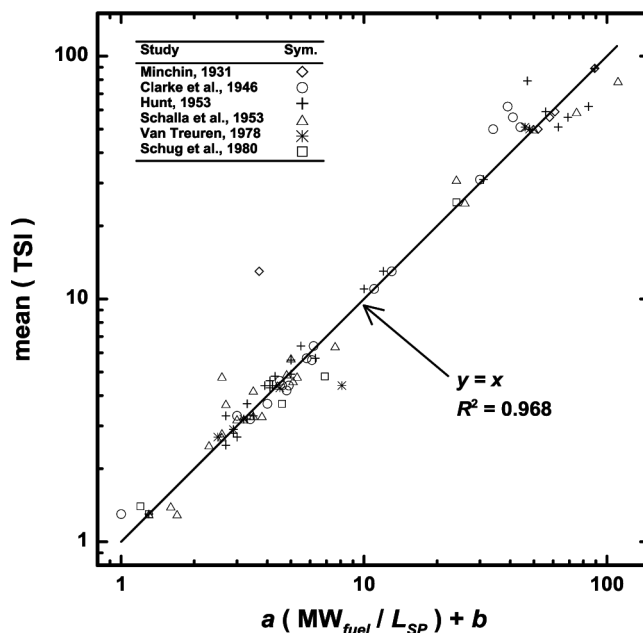


Figure 1 The relationship between arithmetic mean TSI and individual study TSI for hydrocarbons. The quantities shown are from Calcote and Manos (1983). Fuels considered by just one study and/or with negative TSI are excluded.

mean TSI from all studies versus the individual TSI from each study. Figure 1 excludes 56 hydrocarbons for which only one smoke point appeared in the study by Calcote and Manos (1983), because these data fall on the line fit in Figure 1. The use of log axes excludes two additional hydrocarbons with negative TSI values. Figure 1 represents each fuel with symbols at two or more abscissae and at a single ordinate, this being their mean.

NSP NORMALIZATION

An improved normalization of smoke points, called NSP, is introduced here. NSP accounts for systematic differences between studies, e.g., those arising from different fuel and air delivery methods and different smoke detection methods. NSP does not suffer from the five above drawbacks of TSI.

For each fuel, NSP is defined as the weighted average of all the smoke point lengths for that fuel from the 12 studies, i.e.,

$$\text{NSP} = \text{mean} (A L_{SP}) \quad (7)$$

where *mean* is the arithmetic mean and *A* is a dimensionless fitting constant unique to each study. Because the fitting constants *A* would otherwise be underconstrained, it is additionally imposed that

$$\sum_{i=1}^n A_i N_i = \sum_{i=1}^n N_i \quad (8)$$

where i is the study number, N_i is the number of fuels in that study, and n is the total number of studies considered (12 here). Equation (8) ensures that the fitting constants A are close to unity.

For the 12 studies considered, fitting constants A in Equation (7) were optimized such that the R^2 coefficient of determination was maximized in a plot of NSP versus AL_{SP} and such that Equation (8) was satisfied. The resulting plot and fitting constants are shown in Figure 2 and Table 1. The fitting constants are relatively close to unity except for Minchin (1931), whose smoke points were short for unknown reasons. Figure 2 excludes 57 hydrocarbons for which only one smoke point is available, because these data fall on the line fit. Figure 2 represents each fuel with symbols at two or more abscissae and at a single ordinate, this being their mean. Fuels with little or no horizontal scatter about the line fit have sooting propensities that are well captured by the NSP model. Despite the reduction from two fitting constants to one for each study, the R^2 coefficient of determination for the NSP linear fit (Figure 2) is slightly higher than that for TSI (Figure 1). Thus, NSP has statistical success equal to that of TSI while invoking half as many fitting constants.

Table 2 shows the resulting NSP values for the 112 hydrocarbons considered by the 12 studies and the 95% confidence intervals (CI) for fuels considered by more than one study. This is the first time smoke points of so many fuels have been quantitatively related.

Figure 3 plots NSP for the hydrocarbons of Table 2 with respect to C/H, which has been used before to correlate fuel sooting propensities (Allan et al., 2009; Barrientos and Boehman, 2010; Calcote and Manos, 1983; Schug et al., 1980).

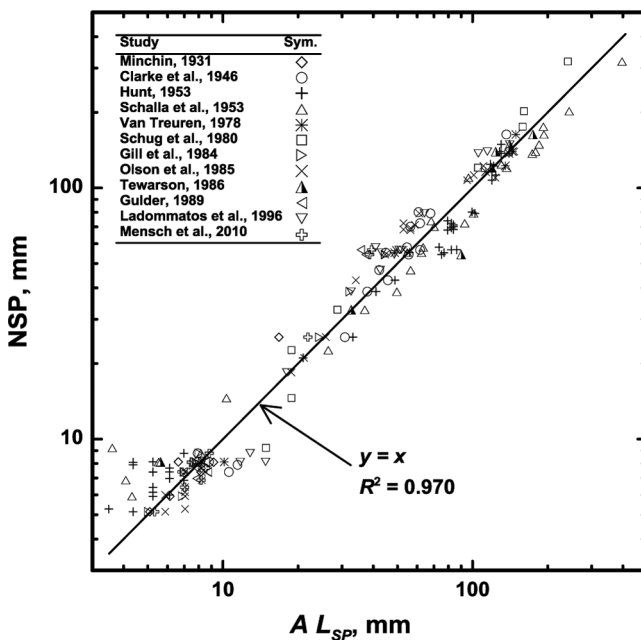


Figure 2 The relationship between NSP and L_{SP} for hydrocarbons. Fuels considered by just one study are excluded.

Table 2 NSP values for 112 hydrocarbons in diffusion flames

Formula	Name	NSP \pm CI ^a , mm	Studies ^b
<i>Alkanes</i>			
C ₂ H ₆	Ethane	319 \pm 153	4,6
C ₃ H ₆	Cyclopropane	25.9	4
C ₃ H ₈	Propane	202 \pm 82	4,6
C ₄ H ₁₀	<i>n</i> -Butane	175 \pm 33	4,6
C ₄ H ₁₀	Isobutane	96.3	4
C ₅ H ₁₀	Cyclopentane	58.0 \pm 13.5	2-4,11
C ₅ H ₁₂	<i>n</i> -Pentane	163 \pm 25	2,4,5,9
C ₅ H ₁₂	Isopentane	104	2
C ₅ H ₁₂	2,2-Dimethylpropane	59.8	4
C ₆ H ₁₂	Methylcyclopentane	55.3 \pm 1.1	3,4
C ₆ H ₁₂	Cyclohexane	81.9 \pm 16.4	2-4,8,9,11
C ₆ H ₁₄	<i>n</i> -Hexane	149 \pm 24	3,4,9,11
C ₆ H ₁₄	2-Methylpentane	116 \pm 7	3,5
C ₆ H ₁₄	3-Methylpentane	124 \pm 12	3,4
C ₆ H ₁₄	2,2-Dimethylbutane	80.1 \pm 38.0	2,3
C ₆ H ₁₄	2,3-Dimethylbutane	105	3
C ₇ H ₁₄	Methylcyclohexane	56.6 \pm 14.2	2,3,8,11,12
C ₇ H ₁₆	<i>n</i> -Heptane	139 \pm 15	2-5,8,9,11
C ₇ H ₁₆	2-Methylhexane	119	3
C ₇ H ₁₆	3-Methylhexane	120	3
C ₇ H ₁₆	2,3-Dimethylpentane	107	3
C ₇ H ₁₆	2,4-Dimethylpentane	102	3
C ₈ H ₁₆	<i>cis</i> -1,3-Dimethylcyclohexane	61.1	3
C ₈ H ₁₆	Ethylcyclohexane	71.3 \pm 24.6	3,8
C ₈ H ₁₆	Cyclooctane	56.4	8
C ₈ H ₁₈	<i>n</i> -Octane	137 \pm 28	3-5,11
C ₈ H ₁₈	2-Methylheptane	120	3
C ₈ H ₁₈	3-Methylheptane	110	3
C ₈ H ₁₈	4-Methylheptane	102	3
C ₈ H ₁₈	3-Ethylhexane	102	3
C ₈ H ₁₈	2,2-Dimethylhexane	87.3	3
C ₈ H ₁₈	2,3-Dimethylhexane	107	3
C ₈ H ₁₈	2,2,4-Trimethylpentane	54.3 \pm 13.0	2,3,7,8-11,12
C ₈ H ₁₈	2,3,4-Trimethylpentane	59.0	2
C ₈ H ₁₈	2,2,3-Trimethylpentane	58.1	2
C ₈ H ₁₈	2-Methyl-3-ethylpentane	89.0	3
C ₉ H ₂₀	<i>n</i> -Nonane	110 \pm 27	4,8
C ₉ H ₂₀	Isononane	129	4
C ₁₀ H ₁₈	Decalin	25.5 \pm 4.3	1,2,3,7,8,12
C ₁₀ H ₂₂	<i>n</i> -Decane	122 \pm 14	3,5,8
C ₁₁ H ₂₄	<i>n</i> -Undecane	113 \pm 23	3,8
C ₁₂ H ₂₂	cyclohexylcyclohexane	42.9 \pm 8.8	2,3,8
C ₁₂ H ₂₆	<i>n</i> -Dodecane	107 \pm 24	3,8
C ₁₃ H ₂₈	<i>n</i> -Tridecane	116	3
C ₁₄ H ₃₀	<i>n</i> -Tetradecane	120	3
C ₁₆ H ₃₄	<i>n</i> -Hexadecane	110	2
C ₁₆ H ₃₄	Isohexadecane	33.2	12
<i>Alkenes</i>			
C ₂ H ₄	Ethene	120 \pm 18	4,6,9
C ₃ H ₆	Propene	32.8 \pm 4.7	4,6,9

(Continued)

Table 2 Continued

Formula	Name	NSP \pm CI ^a , mm	Studies ^b
C ₄ H ₆	1,3-Butadiene	9.23 \pm 11.0	4,6
C ₄ H ₈	1-Butene	29.1	4
C ₄ H ₈	2-Butene	30.7	4
C ₄ H ₈	Isobutene	22.6 \pm 7.4	4,6
C ₅ H ₈	Cyclopentene	10.3	4
C ₅ H ₈	2-Methyl-1,3-butadiene	15.3	11
C ₅ H ₁₀	1-Pentene	47.1 \pm 9.2	2,4,11
C ₆ H ₁₀	Cyclohexene	38.7 \pm 6.3	2-4,7,11
C ₆ H ₁₂	1-Hexene	55.2 \pm 12.5	2-5,11
C ₇ H ₁₂	4-Methylcyclohexene	23.5	8
C ₇ H ₁₄	1-Heptene	70.1 \pm 15.6	2-4
C ₇ H ₁₄	2-Heptene	73.8 \pm 11.0	3,4
C ₈ H ₁₂	1,5-Cyclooctadiene	20.0	8
C ₈ H ₁₄	2,5-Dimethyl-1,5-hexadiene	11.8	4
C ₈ H ₁₆	1-Octene	56.7 \pm 20.9	3,8,10,11
C ₈ H ₁₆	2-Octene	86.4	3
C ₉ H ₁₈	1-Nonene	55.2	8
C ₁₀ H ₁₆	Pinene	18.5	2
C ₁₀ H ₂₀	1-Decene	72.4 \pm 18.0	2-4,8
C ₁₂ H ₂₄	1-Dodecene	68.3 \pm 30.3	3,8
C ₁₃ H ₂₆	1-Tridecene	55.2	8
C ₁₄ H ₂₈	1-Tetradecene	67.9 \pm 22.6	3,8
C ₁₆ H ₃₂	1-Hexadecene	69.2 \pm 25.1	3,8
C ₁₈ H ₃₆	1-Octadecene	82.1	3
<i>1-Alkynes</i>			
C ₂ H ₂	Ethyne	14.6 \pm 8.3	4,6
C ₃ H ₄	Propyne	10.3	4
C ₅ H ₈	1-Pentyne	10.8	4
C ₆ H ₁₀	1-Hexyne	11.0	4
C ₇ H ₁₂	1-Heptyne	18.4 \pm 0.8	8,11
C ₈ H ₁₄	1-Octyne	21.1 \pm 0.2	3,8
C ₁₀ H ₁₈	1-Decyne	23.5	8
C ₁₂ H ₂₂	1-Dodecyne	31.4	3
<i>Aromatics</i>			
C ₆ H ₆	Benzene	8.79 \pm 1.66	2-4,7,11,12
C ₇ H ₈	Toluene	8.12 \pm 1.60	1,2-5,7,8-11,12
C ₈ H ₈	Styrene	5.27 \pm 3.49	3,8
C ₈ H ₁₀	Xylenes	8.10 \pm 1.62	1,2,3,7,8,11,12
C ₈ H ₁₀	Ethylbenzene	5.92 \pm 1.00	1,3,4,7,8
C ₉ H ₈	1-Phenyl-1-propyne	4.70	8
C ₉ H ₈	Indene	5.99 \pm 0.23	3,8
C ₉ H ₁₀	α -Methylstyrene	6.09	10
C ₉ H ₁₂	Mesitylene	5.24	3
C ₉ H ₁₂	Trimethylbenzenes	6.43 \pm 1.17	3,8,12
C ₉ H ₁₂	Cumene	6.14 \pm 1.78	3,8
C ₉ H ₁₂	<i>n</i> -Propylbenzene	6.86 \pm 1.90	3,4,8,12
C ₁₀ H ₈	Naphthalene	3.49	3
C ₁₀ H ₁₀	1,2-Dihydronaphthalene	5.57	12
C ₁₀ H ₁₂	Tetralin	7.40 \pm 1.21	1,2,3,7,8,10,12
C ₁₀ H ₁₄	<i>p</i> -Cymene	7.90 \pm 2.84	2,3,7,8

(Continued)

Table 2 Continued

Formula	Name	NSP \pm CI ^a , mm	Studies ^b
C ₁₀ H ₁₄	<i>n</i> -Butylbenzene	7.39 \pm 2.12	3,8,10
C ₁₀ H ₁₄	<i>sec</i> -Butylbenzene	6.97 \pm 1.69	3,10
C ₁₀ H ₁₄	<i>tert</i> -Butylbenzene	4.37	3
C ₁₀ H ₁₄	Isobutylbenzene	7.41 \pm 2.54	3,10
C ₁₀ H ₁₄	Diethylbenzenes	6.11	3
C ₁₁ H ₁₀	1-Methylnaphthalene	5.14 \pm 0.48	1,3,7,8,12
C ₁₁ H ₁₀	2-Methylnaphthalene	4.37	3
C ₁₁ H ₁₆	<i>sec</i> -Pentylbenzene	6.98	3
C ₁₁ H ₁₆	<i>tert</i> -Pentylbenzene	6.98	3
C ₁₁ H ₁₆	<i>n</i> -Pentylbenzene	10.6	8
C ₁₂ H ₁₂	Dimethylnaphthalenes	4.37	3
C ₁₂ H ₁₆	Cyclohexylbenzene	7.67 \pm 1.06	3,8,10,12
C ₁₂ H ₁₈	Triethylbenzenes	4.37	3
C ₁₂ H ₁₈	<i>m</i> -Diisopropylbenzene	10.6	2
C ₁₃ H ₁₂	Benzylbenzene	4.35	10

^aCI is the 95% confidence interval and is shown for fuels considered by more than one study.

^bStudy numbers correspond to those in Table 1.

The curve fit shown adopts the functional form of Minchin (1931). Smoke points generally decrease with increasing C/H, because C/H increases with fuel carbon atom mole and mass fraction and, generally, with fraction of unsaturated carbon bonds. As previously reported (Glassman, 1989), hydrocarbon sooting propensity

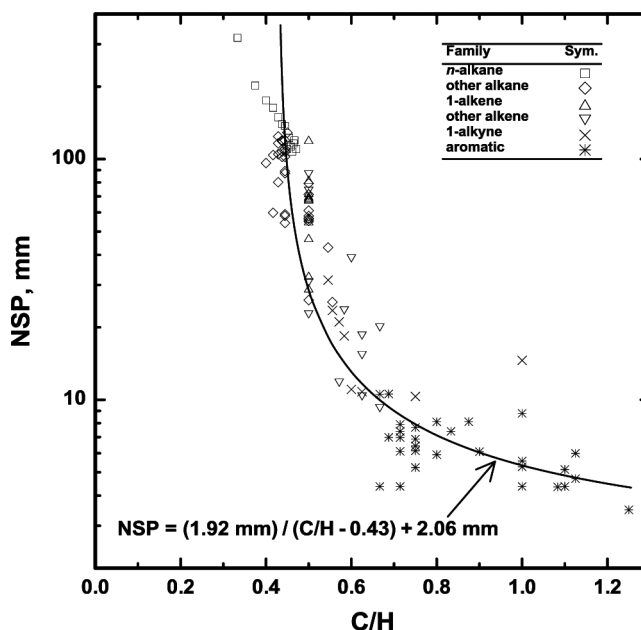


Figure 3 The relationship between NSP and C/H for the 112 hydrocarbons of Table 2.

in diffusion flames is seen to generally increase according to alkanes < alkenes < 1-alkynes < aromatics.

Figure 4 plots NSP for the aliphatic hydrocarbons of Table 2 with respect to carbon number, C , which has been used before to correlate fuel sooting propensities (Allan et al., 2009; Calcote and Manos, 1983; Clarke et al., 1946; Hunt, 1953; Ladommatos et al., 1996; McEnally and Pfefferle, 2007, 2011; Olson et al., 1985; Schalla and McDonald, 1953). For n -alkanes, smoke points generally decrease with increasing carbon number. This is attributed to an accompanying increase in fuel carbon atom mole and mass fraction. There is minimal scatter about the fit shown, which adopts the functional form of Minchin (1931). In contrast to this behavior, smoke points generally increase with increasing carbon number for alkenes and 1-alkynes. This is attributed to an accompanying increased fraction of saturated bonds. Note that TSI results (Calcote and Manos, 1983; Olson et al., 1985) would suggest the opposite trend for alkenes and 1-alkynes, but this is a misleading result arising from the inclusion of MW_{fuel} in Equation (6). In general, Figure 4 shows that n -alkanes have longer smoke points than other alkanes, noncyclic alkenes have longer smoke points than cyclic alkenes, and alkenes with one double bond have longer smoke points than alkenes with multiple double bonds, in agreement with Figure 3 and Clarke et al. (1946) and Olson et al. (1985).

Figure 5 plots NSP for the aromatic hydrocarbons of Table 2 with respect to carbon number. The n -alkane substituted benzenes are connected by dashed lines. These fuels have lower sooting propensity than nearly all other aromatics at corresponding carbon numbers, in agreement with Olson et al. (1985). This is expected when alkane functional groups are added. Fuels with two benzene rings are generally

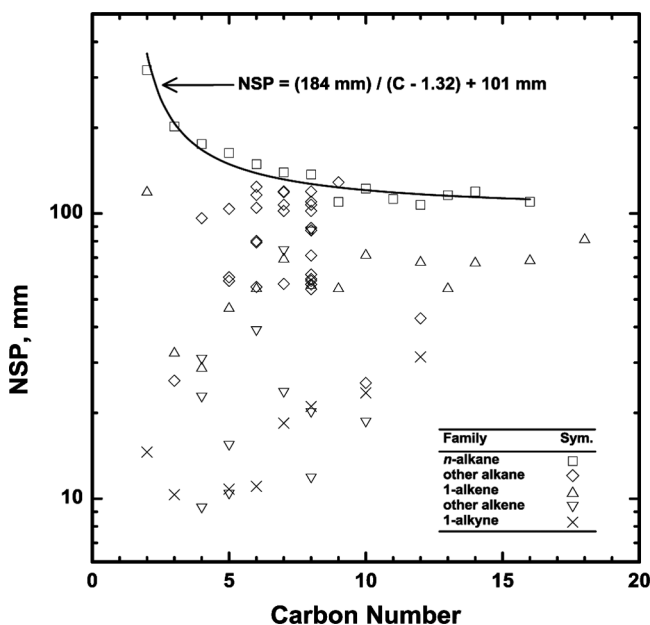


Figure 4 The relationship between NSP and carbon number for the 81 aliphatic hydrocarbons of Table 2.

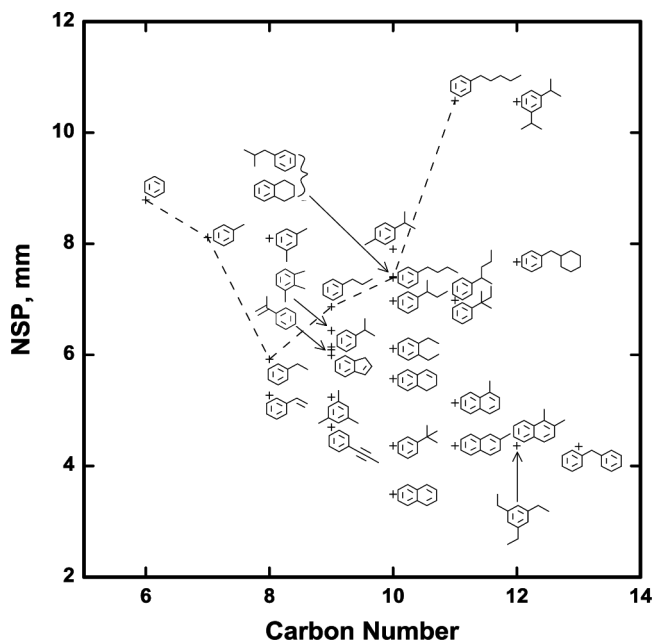


Figure 5 The relationship between NSP and carbon number for the 31 aromatic hydrocarbons of Table 2. The plus symbols identify the values plotted for each fuel.

sootier than those with one ring. While these smoke point properties of aromatics have been reported before, this is the first time they have been demonstrated for so many fuels.

CONCLUSIONS

Having identified problems with the TSI smoke point normalization, an improved smoke point normalization called NSP is presented. NSP values of 112 hydrocarbons were determined. Effects of fuel carbon/hydrogen atom ratio and carbon number on sooting propensity are quantified. The major conclusions are as follows:

1. NSP avoids the major drawbacks of the TSI normalization, particularly the inclusion of fuel molar mass, and yields equal statistics with half as many fitting constants.
2. NSP allows smoke points of 112 fuels, the largest number to date, to be related quantitatively.
3. The sooting propensity of hydrocarbons in diffusion flames generally increases with increasing fuel carbon/hydrogen atom ratio. For *n*-alkanes, sooting propensity increases with carbon number; however it generally decreases with carbon number for alkenes and 1-alkynes.
4. Sooting propensity generally increases according to alkanes < alkenes < 1-alkynes < aromatics. *N*-Alkanes generally have lower sooting propensity than

other alkanes, while 1-alkenes generally have lower sooting propensity than other alkenes.

5. *N*-Alkane substituted benzenes generally have lower sooting propensities than other aromatics, while fuels with two benzene rings are generally sootier than those with just one.

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REFERENCES

- Allan, K.M., Kaminski, J.R., Bertrand, J.C., Head, J., and Sunderland, P.B. 2009. Laminar smoke points of wax candles. *Combust. Sci. Technol.*, **181**, 800–811.
- Barrientos, E.J., and Boehman, A.L. 2010. Examination of the sooting tendency of three-ring aromatic hydrocarbons and their saturated counterparts. *Energy Fuels*, **24**, 3479–3487.
- Beji, T., Zhang, J.P., and Delichatsios, M. 2008. Determination of soot formation rate from laminar smoke point measurements. *Combust. Sci. Technol.*, **180**, 927–940.
- Beji, T., Zhang, J.P., Yao, W., and Delichatsios, M. 2011. A novel soot model for fires: validation in a laminar non-premixed flame. *Combust. Flame*, **158**, 281–290.
- Berry Yelverton, T.L., and Roberts, W.L. 2008. Effect of dilution, pressure, and velocity on smoke point in laminar jet flames. *Combust. Sci. Technol.*, **180**, 1334–1346.
- Calcote, H.F., and Manos, D.M. 1983. Effect of molecular structure on incipient soot formation. *Combust. Flame*, **49**, 289–304.
- Chatterjee, P., de Ris, J.L., Wang, Y., and Dorofeev, S.B. 2011. A model for soot radiation in buoyant diffusion flames. *Proc. Combust. Inst.*, **33**, 2665–2671.
- Clarke, A.E., Hunter, T.G., and Garner, F.H. 1946. The tendency to smoke of organic substances on burning, part 1. *J. Inst. Petrol. Technol.*, **32**, 627–642.
- Dotson, K.T., Sunderland, P.B., Yuan, Z.-G., and Urban, D.L. 2011. Laminar smoke points of coflowing flames in microgravity. *Fire Safety J.*, **46**, 550–555.
- Eddings, E.G., Yan, S., Ciro, W., and Sarofim, A.F. 2005. Formulation of a surrogate for the simulation of jet fuel pool fires. *Combust. Sci. Technol.*, **177**, 715–739.
- Gill, R.J., and Olson, D.B. 1984. Estimation of soot thresholds for fuel mixtures. *Combust. Sci. Technol.*, **40**, 307–315.
- Glassman, I. 1989. Soot formation in combustion processes. *Proc. Combust. Inst.*, **22**, 295–311.
- Gülder, Ö.L. 1989. Influence of hydrocarbon fuel structural constitution and flame temperature on soot formation in laminar diffusion flames. *Combust. Flame*, **78**, 179–194.
- Hunt, R.A. 1953. Relation of smoke point to molecular structure. *Ind. Eng. Chem.*, **45**, 602–606.
- Kewley, J., and Jackson, J.S. 1927. The burning of mineral oils in wick-fed lamps. *J. Inst. Petrol. Technol.*, **13**, 364–382.
- Ladommatos, N., Rubenstein, P., and Bennett, P. 1996. Some effects of molecular structure of single hydrocarbons on sooting tendency. *Fuel*, **75**, 114–124.
- Lautenberger, C.W., de Ris, J.L., Dembsey, N.A., Barnett, J.R., and Baum, H.R. 2005. A simplified model for soot formation and oxidation in CFD simulation of non-premixed hydrocarbon flames. *Fire Safety J.*, **40**, 141–176.

- Lemaire, R., Faccinetto, A., Therssen, E., Ziskind, M., Focsa, C., and Desgroux, P. 2009. Experimental comparison of soot formation in turbulent flames of diesel and surrogate diesel fuels. *Proc. Combust. Inst.*, **32**, 737–744.
- Lemaire, R., Therssen, E., and Desgroux, P. 2010. Effect of ethanol addition in gasoline and gasoline-surrogate on soot formation in turbulent spray flames. *Fuel*, **89**, 3952–3959.
- Li, L., and Sunderland, P.B. 2012. Smoke points of fuel/fuel and fuel/inert mixtures. *Combust. Sci. Technol.* (submitted).
- McEnally, C.S., and Pfefferle, L.D. 2007. Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways. *Combust. Flame*, **148**, 210–222.
- McEnally, C.S., and Pfefferle, L.D. 2009. Sooting tendencies of nonvolatile aromatic hydrocarbons. *Proc. Combust. Inst.*, **32**, 673–679.
- McEnally, C.S., and Pfefferle, L.D. 2011. Sooting tendencies of oxygenated hydrocarbons in laboratory-scale flames. *Environ. Sci. Technol.*, **45**, 2498–2503.
- Mensch, A., Santoro, R.J., Litzinger, T.A., and Lee, S.Y. 2010. Sooting characteristics of surrogates for jet fuels. *Combust. Flame*, **157**, 1097–1105.
- Minchin, S.T. 1931. Luminous stationary flames: The quantitative relationship between flame dimensions at the sooting point and chemical composition, with special reference to petroleum hydrocarbons. *J. Inst. Petrol. Technol.*, **17**, 102–120.
- Olson, D.B., Pickens, J.C., and Gill, R.J. 1985. The effects of molecular structure on soot formation, II: Diffusion flames. *Combust. Flame*, **62**, 43–60.
- Pepiot-Desjardins, P., Pitsch, H., Malhotra, R., Kirby, S.R., and Boehman, A.L. 2008. Structural group analysis for soot reduction tendency of oxygenated fuels. *Combust. Flame*, **154**, 191–205.
- Roper, F.G. 1977. The prediction of laminar jet diffusion flame sizes, part 1: Theoretical model. *Combust. Flame*, **29**, 219–226.
- Schalla, R.L., and McDonald, G.E. 1953. Variation in smoking tendency among hydrocarbons of low molecular weight. *Ind. Eng. Chem.*, **45**, 1497–1500.
- Schug, K.P., Manheimer-Timnat, Y., Yaccarino, P., and Glassman, I. 1980. Sooting behavior of gaseous hydrocarbon diffusion flames and the influence of additives. *Combust. Sci. Technol.*, **22**, 235–250.
- Sunderland, P.B., Mendelson, B.J., Yuan, Z.G., and Urban, D.L. 1999. Shapes of buoyant and nonbuoyant laminar jet diffusion flames. *Combust. Flame*, **116**, 376–386.
- Sunderland, P.B., Mortazavi, S., Faeth, G.M., and Urban, D.L. 1994. Laminar smoke points of nonbuoyant jet diffusion flames. *Combust. Flame*, **96**, 97–103.
- Tewarson, A. 1986. Prediction of fire properties of materials, part 1: Aliphatic and aromatic hydrocarbons and related polymers. Factory Mutual Research, Report NBS-GCR-86-521, MA, USA.
- Urban, D.L., Yuan, Z.-G., Sunderland, P.B., Lin, K.-C., and Faeth, G.M. 2000. Smoke-point properties of non-buoyant round laminar jet diffusion flames. *Proc. Combust. Inst.*, **28**, 1965–1972.
- Van Treuren, K.W. 1978. Sooting characteristics of liquid pool diffusion flames. M.S. Thesis, Princeton University, Princeton, NJ.
- Yan, S., Eddings, E.G., Palotas, A.B., Pugmire, R.J., and Sarofim, A.F. 2005. Prediction of sooting tendency for hydrocarbon liquids in diffusion flames. *Energy Fuels*, **19**, 2408–2415.
- Yang, Y., Boehman, A.L., and Santoro, R.J. 2007. A study of jet fuel sooting tendency using the threshold sooting index (TSI) model. *Combust. Flame*, **149**, 191–205.