



Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale



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ABSTRACT

Databases of sooting indices, based on measuring some aspect of sooting behavior in a standardized combustion environment, are useful in providing information on the comparative sooting tendencies of different fuels or pure compounds. However, newer biofuels have varied chemical structures including both aromatic and oxygenated functional groups, which expands the chemical space of relevant compounds. In this work, we propose a unified sooting tendency database for pure compounds, including both regular and oxygenated hydrocarbons, which is based on combining two disparate databases of yield-based sooting tendency measurements in the literature. Unification of the different databases was made possible by leveraging the greater dynamic range of the color ratio pyrometry soot diagnostic. This unified database contains a substantial number of pure compounds (≥ 400 total) from multiple categories of hydrocarbons important in modern fuels and establishes the sooting tendencies of aromatic and oxygenated hydrocarbons on the same numeric scale for the first time. Using this unified sooting tendency database, we have developed a predictive model for sooting behavior applicable to a broad range of hydrocarbons and oxygenated hydrocarbons. The model decomposes each compound into single-carbon fragments and assigns a sooting tendency contribution to each fragment based on regression against the unified database. The model's predictive accuracy (as demonstrated by leave-one-out cross-validation) is comparable to a previously developed, more detailed predictive model. The fitted model provides insight into the effects of chemical structure on soot formation, and cases where its predictions fail reveal the presence of more complicated kinetic sooting mechanisms. This work will therefore enable the rational design of low-sooting fuel blends from a wide range of feedstocks and chemical functionalities.

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1. Introduction

A sooting tendency is a parameter that characterizes the chemical component of the propensity of a pure compound or fuel mixture to produce soot particles in a combustion environment. It can be measured via several laboratory techniques: these include the height of the smoke point flame when the test fuel is burned in a wick-burner [1], the yield of soot in a flame whose fuel is doped with a small amount of the test fuel [2], and the amount of carbon deposited when the test fuel is pyrolyzed in a packed-bed reactor [3]. Numerous databases have been reported of sooting tendencies measured using these techniques [1–26]. Several semi-empirical predictive models have been developed from these

experimental results that can be used to determine sooting tendencies of compounds that have not been studied experimentally [8,13,17,25,27–30].

The results from these different configurations agree reasonably well, which indicates that sooting tendency is a true fuel property in nonpremixed flames. The underlying chemical mechanism is that different fuels produce different pools of primary reaction products, and these different pools grow to large aromatic hydrocarbons and soot at different rates [2,6,13]. For example, a single-ring aromatic fuel such as toluene will produce aromatic products that can grow directly to two-ring aromatics, whereas an alkane fuel such as *n*-heptane will produce aliphatic products that must grow to single-ring products before they can grow to two-ring aromatics [31]; thus single-ring aromatics have much greater sooting tendencies than alkanes [7].

The sooting tendency of the fuel is important because it strongly affects particulate formation and emissions from practi-

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Table 1

Summary of literature sources of Yield Sooting Indices (YSI), the index (or reference) compounds used to define the YSI scale therein, and the YSI values for the respective index compounds.

Database	Literature sources	Index compounds	Assigned YSI
"High scale"	McEnally and Pfefferle [2], McEnally and Pfefferle [11]	Benzene	30
		Naphthalene	100
"Low scale"	McEnally and Pfefferle [12], Das et al. [22]	<i>n</i> -Hexane	0
		Benzene	100
"Unified scale"	This work	Hexane	30
		Benzene	100

cal combustion devices. For example, the specifications for Jet A aviation fuel include a provision that its smoke point meet certain criteria; the purpose of this provision is to ensure that radiation heat transfer from soot particles does not overheat the combustor liner [32,33]. Similarly, Yang and co-workers found that smoke point sooting tendencies were predictive of particulate concentrations in gas turbine exhausts [10]. In some systems other fuel properties may also affect soot formation, and sooting tendency has to be combined with these other properties to predict emissions. For example, in gasoline direct-injection engines, the fuel volatility affects the degree of mixing during the compression stroke and therefore the amount of particulates formed during the combustion phase; Aikawa and co-workers proposed and validated a quantity called Particulate Mass Index (PMI) to estimate emissions from the joint effects of fuel volatility and sooting tendency [34].

A major challenge for sooting tendency databases and models is the wide range of hydrocarbons found in modern fuels. Petroleum-derived fuels generally contain linear and branched alkanes, alkenes, cycloalkanes, and aromatics [35–37]. Furthermore, these fuels increasingly also contain oxygenated hydrocarbons derived from biomass. Currently most gasoline sold in the United States contains 10 volume % ethanol [38], and most gasoline sold in Brazil has contained 20 vol% or more ethanol for several decades [39]. The US Department of Energy's Co-optimization of Fuels and Engines program – one of the sponsors of this research – is examining the use of fuels with blendstocks other than ethanol. A wide range of promising blendstocks have been identified, including higher alcohols, esters, ethers, furans, and ketones [40].

Unfortunately, all of the existing sooting tendency databases contain either oxygenates or aromatics, but not significant numbers of both. Consequently predictive models of sooting tendency have been explicitly limited to one category or the other. The most significant exception is the work of Ladommatos and co-workers, which contains 3 aromatics (benzene, toluene, and 2-xylene) and 5 alcohols [9]. Similarly, the predictive model of Pepiot-Desjardins et al. [13] is based on a dataset that includes 24 oxygenated hydrocarbons, but only 1 aromatic, 1 alkane, 0 isoalkanes, 0 alkenes, and 0 cycloalkanes. The underlying reason for the absence of this concurrent sooting data is that the sooting tendencies of aromatics and oxygenates differ greatly, which makes it difficult to obtain accurate measurements for both in the same experiment. For example, we have measured sooting tendencies of oxygenates and aromatics in previous work [2,11,12,22], but the results are contained in two incompatible databases due to the limited dynamic range of the laser-induced incandescence diagnostic used in that work.

The objective of the research reported here was to produce a unified sooting tendency database that contains substantial numbers of compounds from all of the categories important in modern fuels – including alkanes, cycloalkanes, aromatics, and oxygenates – and to develop a predictive model applicable to all of them. The database was created by stitching together the two earlier incompatible databases (see Table 1); we have implemented a color-ratio pyrometry diagnostic that has better dynamic range

than the earlier diagnostics [23,41], and used it to measure compounds from both databases in the same set of experiments. In an earlier work we generated a predictive model for sooting tendency based on molecular descriptors [29], however, the increased range of molecular sizes and sooting tendencies in the combined database in this work is better suited to an approach that naturally captures the increase in sooting tendency with an increase in the size of molecules. A new model was developed that is based on decomposing each compound into individual carbon-atom fragments, and assigning a sooting tendency contribution to each fragment based on regression against the unified database. The form of this group contribution model is similar to that used by Pepiot-Desjardins and co-workers to predict sooting tendency [13], and ultimately derives from the approach of Benson to estimating thermodynamic properties [42].

Sooting tendency in this study is defined by the amount of soot produced in a methane/air nonpremixed flame when a small quantity of the test compound of interest is added to the fuel. Since the absolute amount of soot is strongly dependent on the additive concentration and the burner configuration, we linearly rescale the soot concentration into a Yield Sooting Index (YSI) which is essentially independent of experimental details. To do this, we (1) choose two index compounds, *A* and *B*, (2) assign them YSI values, YSI_A and YSI_B , and (3) measure their maximum soot concentration in the flames, $f_{v, \max, A}$ and $f_{v, \max, B}$. Then the YSI for any other test compound *i* is defined by

$$YSI_i = (YSI_A - YSI_B) \times \frac{f_{v, \max, i} - f_{v, \max, B}}{f_{v, \max, A} - f_{v, \max, B}} + YSI_B \quad (1)$$

This procedure is analogous to the octane rating, where the knock intensity measured for a fuel is translated onto a scale where $ON_{\text{heptane}} = 0$ and $ON_{\text{isooctane}} = 100$ [43], and allows us to compare sooting tendencies of compounds whose sooting behavior is too different to be captured in a single experimental configuration. In this study the index compounds are hexane and benzene, and the values assigned to them are $YSI_{\text{hexane}} = 30$ and $YSI_{\text{benzene}} = 100$; the rationale for these choices is discussed in Sections 3.3 and 3.4.

One subtlety of YSI is that the additive concentration can be defined by either the additive mole fraction or mass fraction in the fuel. We will henceforth refer to YSIs determined by these two definitions as YSI-molar and YSI-mass, respectively. YSI-molar is arguably more fundamental and we have used it in our studies of pure hydrocarbons, e.g., [2,11,12,22]. However, adding a specified mole fraction of the test compound requires knowing its average molecular weight; for practical fuels that are complex mixtures of many hydrocarbons, the average molecular weight is typically not known accurately. Thus for these fuels YSI-mass is preferable, and we have used it in our studies of diesel and jet fuel surrogates [24]. Since the current study is focused on pure hydrocarbons, it uses YSI-molar.

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