

Structural group analysis for soot reduction tendency of oxygenated fuels

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Abstract

Oxygenated additives are known to reduce soot formation in diesel engines. Numerous studies, both experimental and numerical, have reported that the reduction of particulate emissions depends on the molecular structure of the additives. In this paper, a structural group contribution approach is proposed to interpret experimental observations on the effect of oxygenated additives on the sooting propensities of hydrocarbon fuels. The statistically based method makes it possible to distinguish between chemical effects caused by the presence of oxygenated groups in the fuel mixture and mere dilution of the original fuel by the additive. The analysis was carried out on several experimental databases encompassing both premixed and nonpremixed configurations that include a new extensive set of smoke point measurements for mixtures of a given fuel with several oxygenated molecules. The current approach unifies the conclusions on the relative efficiency of the various oxygenated functionalities such as alcohols, esters, ethers, and carbonyl groups and provides a potential explanation for the seemingly contradictory trends exhibited by some raw experimental data.

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1. Introduction

1.1. Background and previous observations

Numerous studies have shown that using oxygenated molecules as additives to conventional diesel fuel can considerably reduce the amount of partic-

ulate matter (PM) in the exhaust, with additional potential benefits on NO_x emissions. The chemical mechanisms involved in the soot reduction processes are still not well understood. Among the unanswered questions is the role of the specific structure of the oxygenate molecule. Although the fuel composition has been proven to have a first-order influence on soot production [1–3], conflicting observations have been made about the relative impacts of different oxygenated functional groups. Miyamoto et al. [4,5] showed that the Bosch Smoke (BS) number in the exhaust of a diesel engine was a decreasing func-

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tion of the oxygen mass fraction in the fuel and that the slope of this function was fairly insensitive to the type of oxygenated molecule used as additive. However, Natarajan et al. [6] mentioned that the BS number correlated with exhaust PM, and not necessarily with in-cylinder soot production. Multiple studies of diesel–oxygenate blends in engines have been conducted [6–13], all showing a reduction of particulate matter emissions. The extent of these reductions depended on the oxygen content of the blends, the type of oxygenate used, and the operating conditions of the engine. Overall, the authors consistently noted that fuel properties other than oxygen content should play a role in the soot formation mechanism.

Mueller et al. [14,15] tested DBM and tripropylene glycol methyl ether (TPGME) in a constant-volume combustion vessel and a single-cylinder DI diesel engine and found that the amount of soot produced by the diesel/TPGME blend was half that of the DBM/diesel blend. These results were confirmed by numerical simulations with detailed chemical kinetic mechanisms conducted in the same studies. The simulations indicated that nearly a third of the oxygen contained in the DBM additive was unavailable for soot precursor reduction, and additionally, this additive had a high propensity to form acetylene, a well-known soot precursor. Recently, Westbrook et al. [16] performed simulations of rich premixed homogeneous mixtures of *n*-heptane and oxygenates and found that all additives tested reduced the concentration of soot precursors, but with different efficiencies. For the same mass fraction of oxygen, esters were less effective than alcohols or ethers. This result was explained using the decomposition pattern of the additives. The two oxygen atoms in esters are linked to the same carbon atom and are more likely to form CO₂, whereas if the oxygen atoms are further apart, each of them remains bonded to a different carbon, preventing these carbons from becoming available for soot precursors. Szybist et al. [17] confirmed these observations about ester decomposition with engine studies. On the other hand, Pfefferle and co-workers [18–20] showed in a series of methane diffusion flame experiments that when oxygenates are used as dopants added in very small quantities to the fuel stream, the concentration of soot precursors in the flame actually increases. This surprising difference of behavior between diffusion and premixed flames led Westbrook et al. [16] to conclude that soot production in diesel engines is primarily a premixed combustion problem. Another explanation demonstrated by this study is that methane is a relatively clean fuel, producing very few soot precursors. It will be shown below that adding oxygenates, even in very small quantities, that have longer and more complicated hydrocarbon structures will introduce traces of

larger decomposition products prone to convert into soot precursors.

The observed reduction or increase of PM emissions or soot precursor concentrations can be attributed to various phenomena aside from the modification of the chemistry during the combustion process, including for instance the cetane number, boiling characteristics, or viscosity [21]. Also, many experiments have been conducted using non-negligible amounts of oxygenated additives, from a few percent to sometimes 30% or more oxygen mass fraction in the fuel. Depending on the oxygenate molecule, these oxygen mass fractions can translate into a large liquid volume or mole fraction of additives in the base fuels. Oxygenates are mostly linear or slightly branched paraffins containing oxygen moieties, whereas conventional diesel fuel is a mixture of several hundred hydrocarbon molecules containing about 20% aromatics that are well known for their very strong sooting tendencies. Replacing part of these aromatics by paraffinic chains will decrease soot production, independent of the quantity or nature of the oxygen contained in the additive. To appraise the efficiency of the added oxygen, this dilution effect of replacing highly sooting molecules with clean-burning hydrocarbons must be decoupled from the role of the oxygen itself.

1.2. Group contribution method

Identifying the chemical and physical processes involved in soot formation at the molecular level requires very detailed and exhaustive experimental measurements, such as those of Bönig et al. [22] and Xu et al. [23], that can be used to validate soot formation modeling, as done for example in the work of Appel et al. [24]. However, this level of detail is available only in a limited number of studies, most often in simple, well-controlled configurations. To obtain a broader picture of the efficiency of oxygenated additives, a large number of different molecules and different conditions must be explored, and systematic methods of interpreting the resulting large volume of data are needed. In the present work, a statistical approach based on group contribution theory is proposed as one such method. It does not make an attempt to explain the role of the individual processes contributing to soot formation, such as polycyclic aromatic hydrocarbons formation, nucleation, or surface growth and oxidation. Instead, the proposed method aims at interpreting the experimental data in terms of macroscopic variables such as the structure of the molecules or the amount of oxygen in the fuel. This approach can be used as a screening procedure to identify the most important characteristics of an efficient additive and provide guidelines to set up meaningful, more detailed experiments.

Group contribution methods [25,26] have been used extensively to estimate chemical and physical properties of compounds. Different categories of groups can be defined to describe the structure of a molecule. The early work of Benson et al. [27,28] defines a group as a polyvalent atom with all of its ligands. Joback and Reid [29] consider the type of bonds a polyvalent atom has with its neighbors regardless of the neighbors themselves. The structure-oriented lumping introduced by Quann and Jaffe [30] represents individual hydrocarbon molecules as vectors of incremental structural features. The topological formalism and connectivity indices described in Kier and Hall [31] were used to estimate the physical properties of polymers in [32]. Once a structural description of the molecules is chosen, the contributions of the groups to a given physical or chemical property are estimated through various correlation techniques using available experimental or numerical data. The fitting techniques can be as simple as a linear regression for simple additivity rules [33], or more complex, such as polynomial fitting [34], the UNIFAC group contribution method [35,36], artificial neural networks [37], or multilevel estimation methods [38]. It is interesting to note that the validity of the group contribution method for the given set of data can be rigorously assessed a posteriori using the results of the data fitting.

The reliability of a group contribution method depends largely on the quantity and quality of the available data. A majority of the studies on oxygenated additives mentioned above consider only small samples of oxygenated molecules. Moreover, sooting tendencies are measured using different techniques, over different types of engines and operating conditions. As such, those data are not exploitable for a simple statistical analysis. In this work, a database of smoke point measurements of base fuel/oxygenate blends suitable for such an analysis is created. Smoke point is a good surrogate for actual diesel engine emissions, as its inverse, the threshold sooting index (TSI), correlates very well with actual PM emissions [39]. In the following, the experimental setup and acquisition technique for this previously unpublished database will be described briefly. The smoke point measurements will serve as a basis for presenting the group contribution method adopted in this work and the type of valuable information that can be extracted from the results. To broaden the scope of this analysis, two additional databases are examined in a similar way, namely the simulated soot precursor levels in rich homogeneous reactors using *n*-heptane/oxygenate/air blends from Westbrook et al. [16], and the series of doped methane diffusion flames from Pfefferle and co-workers [18–20]. Although the number of data is limited, and the experimental and modeling uncer-

tainties are non-negligible, results consistently show that oxygen has a beneficial effect on soot emissions, in contrast to some previous claims. Clear trends can be drawn for each of these experimental sets, with ether and alcohol functional groups being more effective than esters for the same quantity of oxygen in the fuel mixture. An interesting feature highlighted by this work is the very high efficiency of ketone and aldehyde groups, although these kinds of molecules have seldom been used in actual engine tests, and rigorous comparison of the carbonyl group to other functional groups such as alcohol, ester, or ether seems to be missing in the literature.

2. Experimental database

Smoke point measurements were performed on an ASTM D1322 standard [40] smoke point test lamp manufactured by Petrolab. A black-painted steel frame was used to house the lamp and reduce air disturbances during measurements. Test procedures followed the ASTM D1322. Kerosene standard was measured prior to any test samples to calibrate the results obtained. At least three readings of the flame height were taken for each sample and then averaged and corrected by the standard measurement. Fuel blends of two base fuels doped with various oxygenated molecules were prepared to provide a range of atomic oxygen concentrations from 0 to 20 wt%. The smoke point of the first desired base fuel, *n*-heptane, was found to be very high (45 mm). It would, therefore, have been impractical as a base fuel for a study investigating potential improvements, and thus increases, in smoke point. Instead, 35 vol% toluene was blended with *n*-heptane and used as a base fuel. The second base fuel was an ultra-low-sulfur BP15 diesel fuel. The various molecules screened are described in Tables 1 and 2. Alcohol, ether, ester, ketone, and aldehyde functional groups are represented, along with mixed alcohol–ether and ester–ether molecules.

The threshold sooting index (TSI) introduced by Calcote and Manos [41] was used instead of the smoke point to analyze the experimental results. TSI is a linear function of the reciprocal of the smoke point (SP) involving the molecular weight (MW) of the molecule:

$$\text{TSI} = a \left(\frac{\text{MW}}{\text{SP}} \right) + b. \quad (1)$$

The *a* and *b* constants are fitted using two reference compounds so that the TSI can be used universally, independent of the apparatus used. The values *a* = 3.32 and *b* = −1.47 proposed by Gill and Olson [42] are used to convert the smoke point measurements into

Table 1
Oxygenated molecules screened in the smoke point experiments—Part I

Name	Short name	Formula	Structure	Functional groups	MW [g/mol]	ρ_{liq} [kg/L]
<i>n</i> -Heptane	NC ₇	C ₇ H ₁₆		Alkane	100	0.68
Toluene	TOL	C ₇ H ₈		Aromatic	92	0.86
Methanol	MeOH	CH ₄ O		Alcohol	32	0.787
Ethanol	EtOH	C ₂ H ₆ O		Alcohol	46	0.787
Butanol	ButOH	C ₄ H ₁₀ O		Alcohol	74	0.81
Hexanol	HexOH	C ₆ H ₁₄ O		Alcohol	102	0.81
Octanol	OctOH	C ₈ H ₁₈ O		Alcohol	130	0.824
Diethyl ether	DEE	C ₄ H ₁₀ O		Ether	74	0.71
Dimethoxymethane	DMM	C ₃ H ₈ O ₂		Ether	76	0.86
Diglyme	DEGDE	C ₆ H ₁₄ O ₃		Ether	134	0.95
Monomethyl ether	DEGME	C ₅ H ₁₂ O ₃		Ether, alcohol	120	1.04
2,2-Dimethoxypropane	2,2DMP	C ₅ H ₁₂ O ₂		Ether	104	0.85
Methyl acetate	MA	C ₃ H ₆ O ₂		Ester	74	0.932
Ethyl acetate	EA	C ₄ H ₈ O ₂		Ester	88	0.897
Methyl propanoate	MP	C ₄ H ₈ O ₂		Ester	88	0.91
Ethyl propanoate	EP	C ₅ H ₁₀ O ₂		Ester	102	0.884
Methyl butanoate	MB	C ₅ H ₁₀ O ₂		Ester	102	0.893
Ethyl butanoate	EB	C ₆ H ₁₂ O ₂		Ester	116	0.874
Diethyl carbonate	DC	C ₅ H ₁₀ O ₃		Ester	118	0.97

TSI. The introduction of the molecular weight offsets the minor flame height increase caused by the increased fuel molecular weight, which requires a larger air/fuel volume ratio for stoichiometric combustion. TSI was preferred over smoke point because of its simple mixing rule [42],


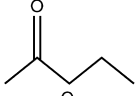
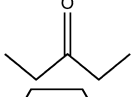
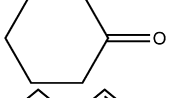

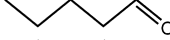

$$\text{TSI}_{\text{mix}} = \sum_k X_k \text{TSI}_k. \quad (2)$$

In this equation, TSI_{mix} is the TSI of the mixture, and X_k and TSI_k are the mole fraction and the TSI of the

pure component k , respectively. A fuel with a strong sooting tendency will have a small smoke point and conversely a large TSI. The experimentally measured TSIs are presented in Figs. 1 and 2.

The larger the amount of oxygen in the mixture is, the smaller the TSI is. For the same mass fraction of oxygen in the mixture, very different levels of improvement can be obtained. Additives such as aldehydes or long-chain alcohols are seemingly the most effective compared to other types of functional groups such as esters or ethers. However, part

Table 2
Oxygenated molecules screened in the smoke point experiments—Part II

Name	Short name	Formula	Structure	Functional groups	MW [g/mol]	ρ_{liq} [kg/L]
Acetone	Acetone	C ₃ H ₆ O		Ketone	58	0.79
2-Pentanone	2PentCO	C ₅ H ₁₀ O		Ketone	86	0.802
3-Pentanone	3PentCO	C ₅ H ₁₀ O		Ketone	86	0.815
Cyclohexanone	CHexCO	C ₆ H ₁₀ O		Ketone	98	0.942
Butanal	ButCOH	C ₄ H ₈ O		Aldehyde	72	0.80
Pentanal	PentCOH	C ₅ H ₁₀ O		Aldehyde	86	0.805
Hexanal	HexCOH	C ₆ H ₁₂ O		Aldehyde	100	0.81

of the TSI improvement comes from the replacement of some of the highly sooting aromatic components in the base mixture by linear substituted alkanes that burn cleaner. The importance of this dilution effect is illustrated by the following example. Consider the sooting tendency of three mixtures: the pure *n*-heptane/toluene base fuel, a mixture of base fuel and a certain volume of hexanol corresponding to $Y_{\text{O}} = 4.1\%$, and a mixture of base fuel and the same volume of *n*-heptane. Resulting TSI and mass fraction of carbon from straight aliphatic chains, $Y_{\text{C,lin}}$, are shown in Table 3 for the three mixtures. In this table, V_{A} is the additive volume fraction, X_{NC_7} , X_{TOL} , and X_{OH} are the mole fractions of *n*-heptane, toluene, and hexanol, respectively. TSIs for the base fuel and hexanol/base fuel mixture are taken directly from experiments. The TSI of the *n*-heptane-substituted mixture is evaluated using the TSI mixing rule shown in Eq. (2). The hexanol mixture has a TSI value 20% lower than the initial *n*-heptane/toluene base fuel. However, the *n*-heptane-substituted mixture presents a 12.5% improvement compared to the initial fuel, solely because part of the toluene has been replaced by a straight-chain alkane. The mass fraction of carbon contained in the aliphatic part of the mixture is similar for hexanol- and *n*-heptane-substituted mixtures, so that the difference of TSIs between these mixtures can be attributed to the sole presence of oxygen. Thus, the oxygen in the alcohol molecule accounts for about a third of the total TSI improvement only, and the remaining contribution comes from the dilution of toluene by alkanes.

The decoupling between dilution and oxygen effects can be done directly only for a few simple cases, such as the previous example, when data for alkanes with the same structure as the oxygenated molecule are available. The goal of the present work is to use structural group analysis to quantify in a systematic fashion the effect of each oxygenated moiety on the sooting tendency of a fuel, independent of the hydrocarbon part of the molecule. This analysis will provide two additional outcomes: first, it will give a strategy to estimate the sooting tendency of a molecule for which no experimental data are known. Second, it will provide theoretical insights into how to combine hydrocarbon parts and oxygen moieties in a molecule to get the largest reduction in sooting tendency for the configurations considered in the study.

3. Interpretation of smoke point database using a statistical approach

3.1. Group additivity theory

The group additivity theory introduced by Benson et al. [27,28] was developed initially to estimate thermodynamic properties of molecules for which no data were available. This technique considers nearest-neighbor interactions to estimate group contributions. The molecule is decomposed into groups defined as polyvalent atoms with all their ligands. This group definition is adopted here, and the groups are represented following Benson's notation. The polyvalent atom is written in bold face, and its ligands are

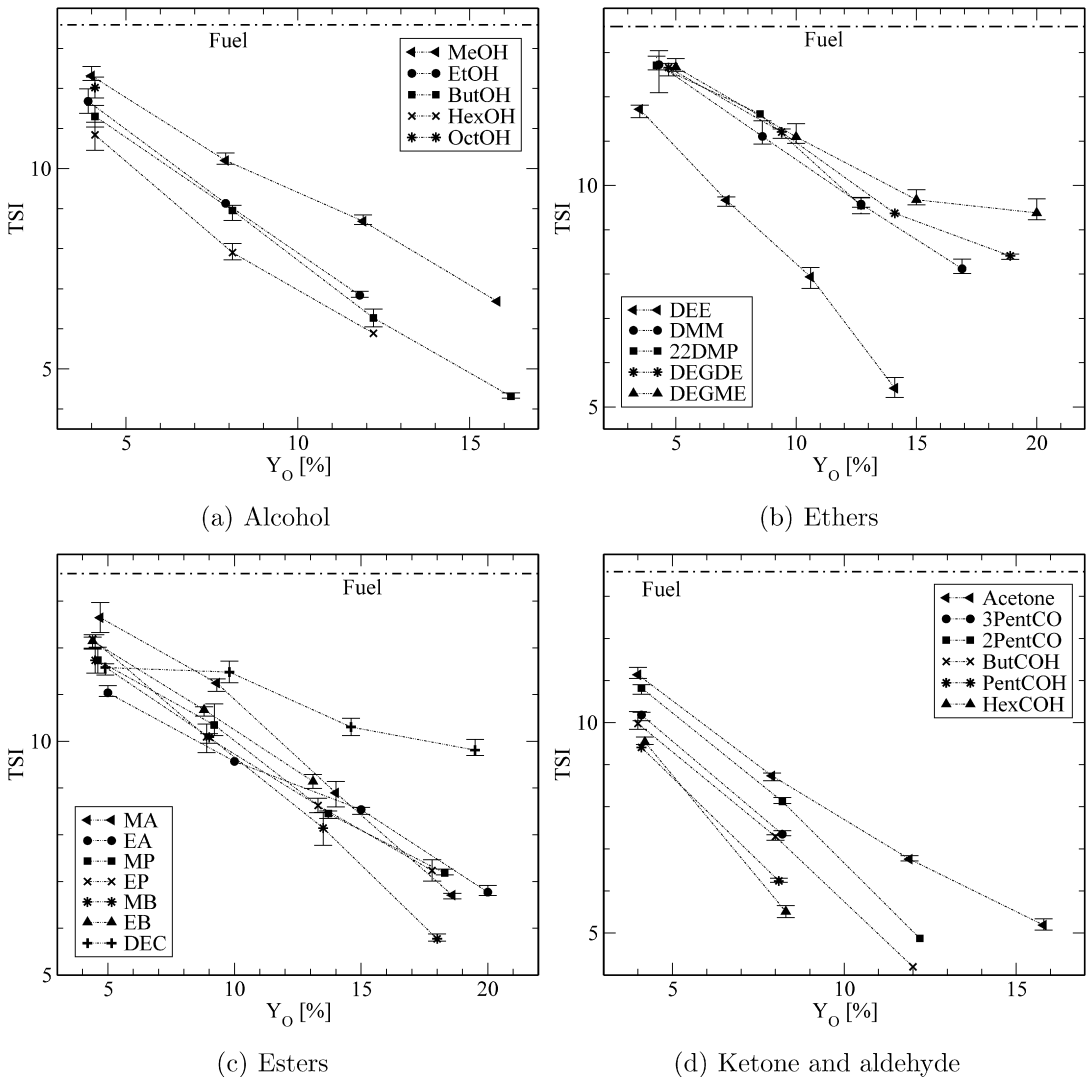


Fig. 1. Experimental threshold soot indices for oxygenates/*n*-heptane/toluene mixtures.

specified between brackets, after a dash. For example, a carbon atom linked to an oxygen atom and three hydrogens is written as C-(O)(H)₃. The base fuels, either the *n*-heptane/toluene mixture or the BP15 diesel fuel, are treated as a single lumped group. The groups are defined in Table 4. As stated in [27], the carbonyl group is treated as a single group, and the methyl groups C-(C)(H)₃, C-(O)(H)₃, and C-(CO)(H)₃ are not distinguished. Also, the limited number of molecules and types of groups available in the TSI database requires that some groups be combined into generic or multiatom groups, such as the ester group.

Two main classes can be identified: the end-groups, such as C-(C)(H)₃ (#3), that appear at the end of a chain, and the midgroups, such as C-(C)₂(H)₂

(#6), that refer to polyvalent atoms appearing inside a chain. This distinction is important, since an oxygenated end-group efficiency cannot be compared to the efficiency of a hydrocarbon midgroup. The former cannot be substituted for the latter. Also recorded in Table 4 is the number of occurrences of each group in the database. The larger this number is, the higher is the confidence in the group contribution. A few specific groups appear in a single molecule only, and therefore are associated with a higher uncertainty as to their contribution.

The TSI mixing rule, which was defined for multicomponent fuel mixtures in Eq. (2), can be extended easily to the group level. The TSI of a mixture is expressed as a linear combination of the TSI contribution of each group in the mixture with a weighting fac-

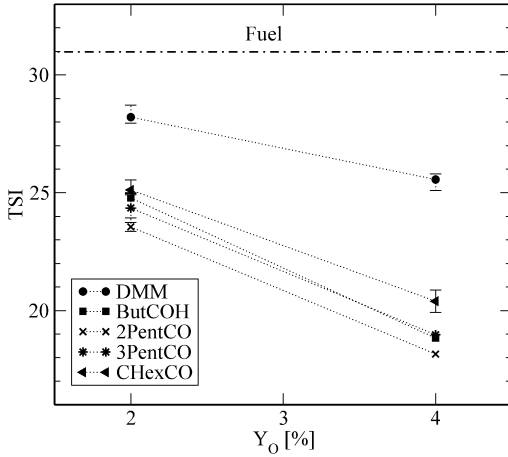


Fig. 2. Experimental threshold soot indices for oxygenates/diesel mixtures.

Table 3
Illustration of the importance of the dilution effect

Additive	V _A	X _{NC7}	X _{TOL}	X _{OH}	Y _{C,lin} [%]	TSI
None	0.0	0.5738	0.4261	0.0	57.38	13.61 ^a
Hexanol	0.2448	0.4295	0.3190	0.2514	66.91	10.86 ^a
<i>n</i> -Heptane	0.2448	0.6687	0.3313	0.0	66.86	11.90 ^b

^a Experimental data.

^b Estimated using Eq. (2).

tor proportional to the mole fraction of the molecule and the number of groups in this molecule:

$$\widetilde{TSI} = \sum_{i=1}^{n_S} X_i \left(\sum_{j=1}^{n_{G,i}} N_{j,i} C_j^{TSI} \right). \quad (3)$$

In this equation, \widetilde{TSI} is the estimated TSI of the mixture, n_S is the number of species in the mixture, $n_{G,i}$ is the number of groups in species i , $N_{j,i}$ is the number of group of type j in species i , and C_j^{TSI} is the contribution of group j to TSI.

The coefficients C_j^{TSI} for each group are computed through least-squares fitting of the experimental data, expressed as the optimization problem

$$\min \chi^2 = \sum_{k=1}^{n_{\text{exp}}} \left(\frac{TSI_k^{\text{exp}} - \widetilde{TSI}_k}{\sigma_k} \right)^2, \quad (4)$$

where the standard deviation σ_k is estimated from the multiple measurements of each mixture k .

It must be emphasized that the assumption made in this analysis is that the data on threshold sooting indices can be described with good accuracy by Eq. (3), which is based on the structural contributions of the fuel only. This assumption will be validated by comparing the actual data with the estimated val-

Table 4
Structure, occurrences, and contribution of the groups in the TSI correlation study

Group	ID	Type	Occurrences	Contribution
Hept./tol.	0	Base fuel	77	13.5295 ^a
Diesel	1	Base fuel	10	31.2279 ^b
C-(C)(H) ₃				
C-(O)(H) ₃	3	End	148	1.4827
C-(CO)(H) ₃				
O-(C)(H)	4	End	19	0.2772
CO-(C)(H)	5	End	9	-2.9917
C-(C) ₂ (H) ₂	6	Mid	59	0.3186
C-(C)(O)(H) ₂	7	Mid	70	0.2624
C-(C)(CO)(H) ₂	8	Mid	41	-0.5947
C-(O) ₂ (H) ₂	9	Mid	6	0.9712
O-(C) ₂	10	Mid	42	-0.8028
CO-(C) ₂	11	Mid	15	-1.728
COO-(C) ₂	12	Mid	23	-1.8438
COOO-(C) ₂	13	Mid	4	0.2111
C-(C) ₂ (O) ₂	15	Mid	3	1.5502
Ring	16	Mid	2	6.1196

^a TSI_{exp} = 13.61.

^b TSI_{exp} = 30.98.

ues computed from Eq. (3). Also, it is worth noting that the physical and thermodynamic properties of the fuel, which vary for each oxygenated mixture, are very accurately described by structural group analysis. Therefore, these properties are inherently embedded in the analysis, and do not introduce additional degrees of freedom.

3.2. Correlation results

Fig. 3 shows the experimental TSI measurements versus the estimated TSIs computed using Eq. (3) and the values for the group contributions obtained through the optimization procedure. The correlation coefficient is nearly 99%, the maximum error is 14.6%, while the average error is only 4.15%. A good correlation is obtained regardless of the type of base fuel, thereby validating the assumption stated by Eq. (3). The lowest TSI values are obtained with the *n*-heptane/toluene base fuel mixtures; the highest values are obtained with diesel fuel mixtures. Better correlations could be obtained by using more complicated fitting expressions such as polynomials. For example, Yan et al. [43] successfully used fourth-order polynomial fitting to correlate the TSIs of hydrocarbon molecules. However, the introduction of nonlinear fitting terms would render the direct analysis of the contribution coefficients more difficult. In this respect, the small loss of accuracy introduced by the lower order fitting function is justified, considering the purpose of this work.

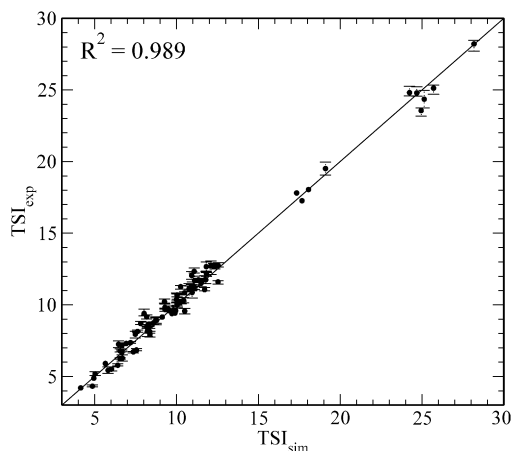


Fig. 3. Correlation between experimental TSIs and TSIs simulated using Eq. (3). Error bars correspond to experimental uncertainties.

The value of the group coefficients are shown in Table 4. The contributions from the base fuels are determined by the fitting procedure, but in both cases these contributions are very close to the experimental values. The very good agreement for the base fuels confirms that the linear mixing rule is appropriate for TSI.

The three groups in the end-group subset, namely methyl (#3), alcohol (#4), and aldehyde (#5) groups, are interchangeable, and therefore, can be compared with each other. Clearly, replacing a methyl group with either of the two oxygenated groups results in a substantial improvement in the sooting tendency. The aldehyde group has the greatest impact, as its contribution is largely negative. This beneficial effect is amplified if the adjacent midgroup is considered. Indeed, the variety of oxygenated molecules makes it possible to distinguish between a C atom sitting next to another C (#6), an O (#7), or a carbonyl group (#8). Results show that a C atom next to an alcohol group (i.e., #7 next to #4), has a smaller coefficient than a C atom in a hydrocarbon chain (i.e., #6 next to #3), and that a C atom next to a carbonyl group (i.e., #8 next to #5) even has a negative contribution to the TSI of the mixture.

The contribution of the midgroups should be compared to the value of the midgroup C-(C)₂(H)₂ (#6). All oxygenated midgroups have beneficial effects on the TSI, with the ester group having the most negative contribution. However, if the contributions are given per O atom, the carbonyl group in ketones is clearly the most powerful, its effect being amplified by the negative contribution of the group C-(C)(CO)(H)₂ (#8), to which the carbonyl group is linked most often. The next most efficient group is the ether group, closely followed by the ester group. The diester group

(#13), present in this study in diethyl carbonate, only introduces a slight improvement in sooting tendency. Having two ether groups close together with only one C atom between them offsets part of the benefits of the oxygen, because of the relatively large positive contribution of the group C-(O)₂(H)₂ (#9) compared to the small contribution of C-(C)(O)(H)₂ (#7). This effect was observed by Cheng and Dibble [44], who performed experiments with DMM and DEE. For the same oxygen mass fraction in the diesel blend, DMM, which contains group #9, was slightly less efficient at decreasing PM emissions than DEE, which contains group #7. However, DEE contains half the amount of oxygen of DMM, and thus requires twice the amount of additive for a similar PM reduction.

Branching tends to increase sooting tendency significantly. Replacing a midgroup C-(C)₂(H)₂ (#6) with the branching group C-(C)₂(O)₂ (#15) multiplies the contribution of the group by 5; introducing a ring (#16), as in cyclohexanone, multiplies this contribution by nearly 20. Although the number of experiments available for these types of groups is small, the effect is large enough to allow the conclusion, supported by previous work (for example, Gomez et al. [45]), that branched molecules have a stronger tendency to produce soot than linear ones.

3.3. Comparison between dilution effect and oxygen efficiency

In this section, the relative magnitudes of the dilution and oxygen effects are discussed. The groups are distributed into three distinct sets: the hydrocarbon groups, $\{\mathcal{H}\} = \{3, 6, 15, 16\}$, the oxygenated end-groups, $\{\mathcal{O}_E\} = \{4, 5\}$, and the oxygenated midgroups, $\{\mathcal{O}_M\} = \{7, 8, 9, 10, 11, 12, 13\}$. The change in TSI due to dilution can be defined as the improvement that comes from the replacement of a part of the base fuel by the additive, in which all oxygen groups have been replaced by the corresponding end or midhydrocarbon groups (groups #3 or #6). This change can be written as

$$\Delta\text{TSI}_D = X_A \left(\sum_{j \in \{\mathcal{H}\}} N_{A,j} C_i + \sum_{j \in \{\mathcal{O}_E\}} N_{A,j} C_3 + \sum_{j \in \{\mathcal{O}_M\}} N_{A,j} C_6 - C_{\text{fuel}} \right). \quad (5)$$

The TSI improvement due to oxygen can be defined as the difference between the contribution from the oxygenated groups and the contribution from the corresponding hydrocarbon groups. This term is evaluated through the expression

$$\Delta\text{TSI}_O = X_A \left(\sum_{j \in \{\mathcal{O}_E\}} N_{A,j} (C_i - C_3) \right)$$

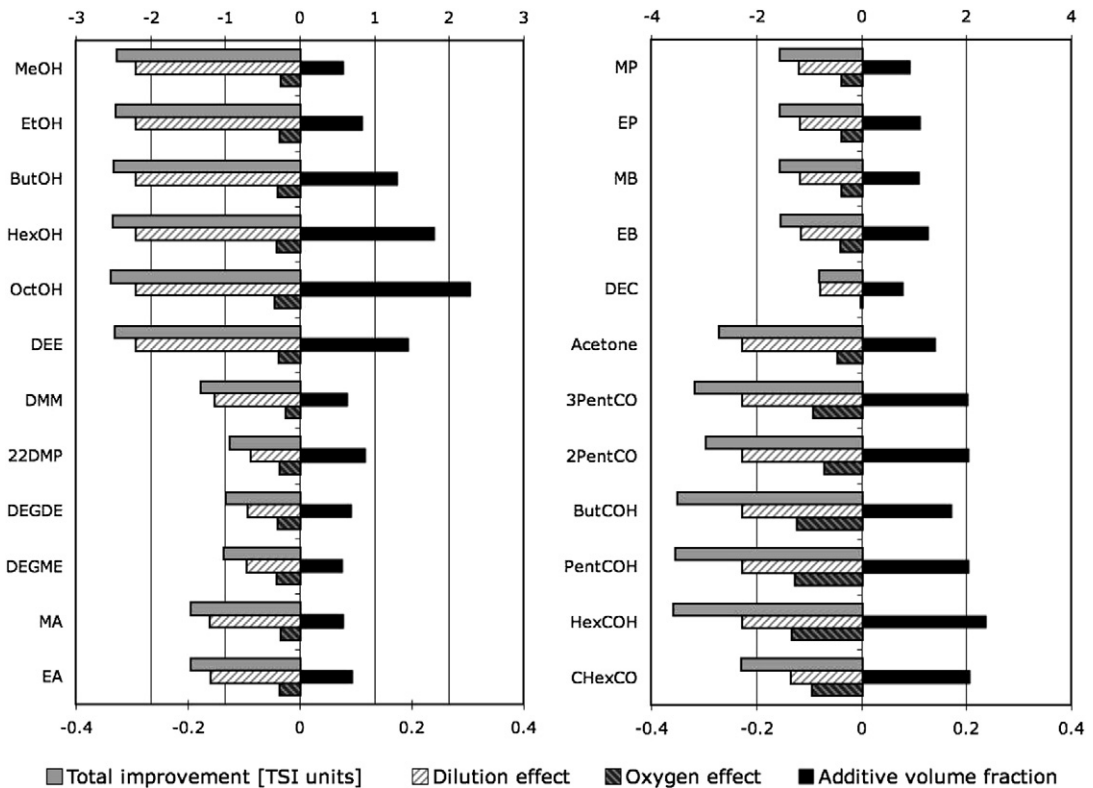


Fig. 4. Contribution of dilution and oxygen in total TSI improvement (top axis) and corresponding volume of additive (bottom axis).

$$+ \sum_{j \in \{O_M\}} N_{A,j} (C_i - C_6) \Big) \tag{6}$$

The total TSI improvement is the sum of both contributions, namely

$$\Delta TSI = \Delta TSI_D + \Delta TSI_O \tag{7}$$

The contributions from Eqs. (5), (6), and (7) are evaluated for each molecule screened in this study, and for a constant mass fraction of oxygen: $Y_O = 4\%$. The results are shown in Fig. 4, along with the corresponding volume fraction of additive in the base fuel. The high efficiency of the alcohol molecules comes primarily from dilution, whereas the best ratio between dilution and oxygen efficiency is found in the aldehyde and ketone molecules. The model also predicts for both linear alcohols and aldehydes that the shorter-chain molecules are better. Although, for these molecules, the total TSI improvement is similar, the volume of additive needed to reach a constant oxygen mass fraction is smaller for shorter molecules.

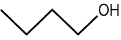
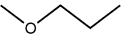
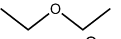
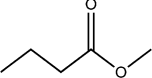
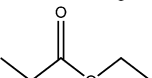
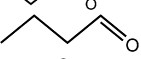
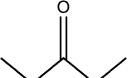
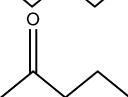
3.4. Comparison of similar additive molecules

The structural analysis of the TSI measurements gives a precise estimate of the efficiency of the dif-

ferent oxygenated functional groups. It also allows us to simulate the efficiency of any molecule that can be built from groups for which a contribution was determined. In the following, pentane is compared to structurally similar molecules obtained by substituting a carbon group by an oxygenated group. First, the TSI of the oxygenate/base fuel blend is computed for a constant mass fraction of oxygen in the mixture, $Y_O = 4\%$, that corresponds to a volume V_A of oxygenate. Then, the TSI of a pentane/base fuel blend containing the same volume V_A of pentane is computed. The improvement of using the oxygenate over the straight-chain alkane is evaluated. Results are shown in Table 5. In this table, V_A is the additive, either oxygenate or pentane, volume fraction, TSI_O is the TSI of the oxygenate substituted mixture, and TSI_{C_5} is the TSI of the mixture containing pentane. The last column gives the additional relative benefit to TSI when the oxygenated molecule is used instead of pentane.

At a constant mass fraction of oxygen, the efficiency of the functional groups compared to straight-chain hydrocarbons can be ranked as follows: alkanes, esters, ethers, alcohols, ketones, and aldehydes. However, because of the number of O atoms in the additive

Table 5
Relative efficiency of oxygenated additives compared to pentane in TSI experiments

Additive	Formula	Structure	V_A	TSI_O	TSI_{C_5}	Improvement
Butanol	$C_4H_{10}O$		0.1739	11.04	11.70	−5.62%
Methoxypropane	$C_4H_{10}O$		0.1900	11.06	11.53	−4.09%
Diethyl ether	$C_4H_{10}O$		0.1933	11.04	11.50	−3.92%
Methyl butanoate	$C_5H_{10}O_2$		0.1089	11.99	12.37	−3.14%
Ethyl propanoate	$C_5H_{10}O_2$		0.1099	11.98	12.36	−3.11%
Pentanal	$C_5H_{10}O$		0.2027	9.99	11.40	−12.33%
3-Pentanone	$C_5H_{10}O$		0.2017	10.35	11.41	−9.28%
2-Pentanone	$C_5H_{10}O$		0.2033	10.57	11.39	−7.26%

molecule, esters require about half the volume of additive to achieve the oxygen mass fraction. Actually, looking at a constant volume fraction of additive, ester molecules are slightly more efficient than ethers.

4. Analysis of other databases

The goal of this section is to extend the structural group analysis to other published databases. Because the method requires a sufficiently large set of data to be applicable, few exploitable studies were found. The first one is a numerical study by Westbrook et al. [16] of soot precursor concentration in a homogeneous, fuel-rich environment. The second one is a collection of methane diffusion flames doped with various oxygenated fuels by Pfefferle et al. [18–20].

4.1. Simulated data of soot precursor concentration reduction in homogeneous configurations

Westbrook et al. [16] conducted a numerical study of the effect of oxygenate additives on the formation of soot precursors in a rich, homogeneous reactor. The base fuel is *n*-heptane and the oxygenated molecules used in the study are described in Table 6. The percentage of initial carbon mass present in the soot precursor species at the end of the simulation is computed as a function of the mass fraction of oxygen in the *n*-heptane/oxygenate mixture. These percentages steadily decrease as the oxygen mass fraction increases. The slope of the decrease depends on the type of oxygenate added to the initial *n*-heptane fuel.

The groups used for the structural analysis are presented in Table 7 and are similar to those used above. The modeling assumption is written as:

$$\tilde{M}_{C,SP} = \sum_{i=1}^{n_S} X_i \left(\sum_{j=1}^{n_{G,i}} N_{j,i} C_j^{M_{C,SP}} \right), \quad (8)$$

where $\tilde{M}_{C,SP}$ is the estimated mass of carbon in the soot precursor species, and $C_j^{M_{C,SP}}$ is the contribution of group *j* to $M_{C,SP}$. The correlation results are shown in Fig. 5. The correlation parameter R^2 is more than 0.997 with a maximum error of 8.4% and an average error of 2.0%. The errors are small for all mixtures included in the analysis, which confirms the validity of the assumption stated in Eq. (8). The group contributions are indicated in Table 7. The oxygenated groups overall reduce the quantity of soot precursors produced in the mixture during ignition, as they all have a negative contribution.

Comparison of the efficiency of each group can be done by comparing pentane with oxygenates having a similar structure, namely butanol, methoxypropane, and methyl butanoate. To do so, the mass of carbon in soot precursors is computed using Eq. (8) for rich mixtures ($\Phi = 3$) of *n*-heptane/oxygenate/air for a constant mass fraction of oxygen in the fuel/oxygenate mixture: $Y_O = 4\%$. Then an equal mole fraction of pentane is substituted for the oxygenates and the mass of carbon in the soot precursors is recomputed and compared. The various mixtures have an initial mass of carbon that differs by a few percent only. This effect can be neglected when compared to the difference of efficiencies observed. The improvement of using

Table 6

Oxygenated molecules screened in Westbrook et al.'s [16] numerical study of *n*-heptane autoignition

Name	Short name	Formula	Structure	Functional groups	MW [g/mol]
Methanol	MeOH	CH ₄ O		Alcohol	32
Ethanol	EtOH	C ₂ H ₆ O		Alcohol	46
Dimethyl ether	DME	C ₂ H ₆ O		Ether	46
Dimethoxymethane	DMM	C ₃ H ₈ O ₂		Ether	76
Methyl butanoate	MB	C ₅ H ₁₀ O ₂		Ester	102
Tripropylene glycol methylether	TPGME	C ₁₀ H ₂₂ O ₄		Ether, alcohol	206
Diethyl carbonate	DC	C ₅ H ₁₀ O ₃		Ester	118
Dibutyl maleate	DBM	C ₁₂ H ₂₀ O ₄		Ester	228

Table 7

Structure, occurrences, and contribution of the groups in Westbrook et al.'s [16] numerical study of *n*-heptane autoignition

Group	ID	Type	Occurrences	Contribution
C-(C)(H) ₃	3	End	50	2.03662
C-(O)(H) ₃				
O-(C)(H)	4	End	9	-8.67932
C-(C) ₂ (H) ₂				
C-(C)(O)(H) ₂	6	Mid	51	6.45243
C-(C)(CO)(H) ₂				
O-(C) ₂	10	Mid	17	-6.57876
COO-(C) ₂	12	Mid	11	-5.03328
COOO-(C) ₂	13	Mid	4	-10.45359
C-(C) ₃ (H)	14	Mid	9	5.20552
C-(C)(CO)(H)	17	Mid	8	5.93949

oxygenates instead of alkane is summarized in Table 8. The alcohol group appears to be more efficient than the ether group, which itself is more efficient than the ester group for a given oxygen mass fraction. The same order is recovered when the mixtures are compared at constant mole fraction of additive. This ranking is consistent with the observations made on the smoke point database.

4.2. Methane diffusion flames with oxygenated dopants

Pfefferle et al. [18–20] published a series of methane-doped flames, in which products were measured using mass spectrometry. The following analysis correlates the maximum amount of aromatic species

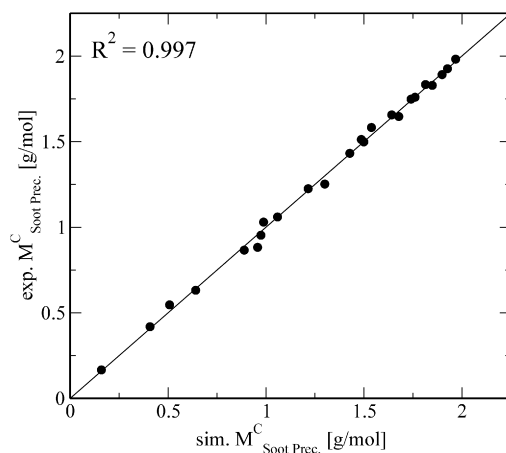


Fig. 5. Correlation between experimental and simulated carbon mass in soot precursors species in Westbrook et al.'s [16] numerical study of *n*-heptane autoignition.

Table 8

Relative efficiency of oxygenated additives compared to pentane in Westbrook et al.'s [16] numerical study of *n*-heptane autoignition

Additive	Formula	X _A	Improvement
Butanol	C ₄ H ₁₀ O	0.01414	-16.65%
Methoxypropane	C ₄ H ₁₀ O	0.01414	-9.18%
Methyl butanoate	C ₅ H ₁₀ O ₂	0.00713	-4.15%

measured in the flame with the initial composition of the mixture. The aromatic species include benzene, toluene, phenylacetylene, styrene, and naphthalene. Due to experimental uncertainties, there are some discrepancies between the maximum mole fraction

Table 9
Oxygenated molecules screened in Pfefferle et al.'s [18–20] study of CH₄ diffusion flames

Name	Short name	Formula	Structure	Functional groups	MW [g/mol]
Butane	NC ₄	C ₄ H ₁₀		Alkane	58
<i>iso</i> -Butane	IC ₄	C ₄ H ₁₀		Alkane	58
Butanol	ButOH	C ₄ H ₁₀ O		Alcohol	74
2-Butanol	2ButOH	C ₄ H ₁₀ O		Alcohol	74
<i>iso</i> -Butanol	iButOH	C ₄ H ₁₀ O		Alcohol	74
<i>tert</i> -Butanol	tButOH	C ₄ H ₁₀ O		Alcohol	74
Methyl butanoate	MB	C ₅ H ₁₀ O ₂		Ester	102
Methyl isobutyrate	MIB	C ₅ H ₁₀ O ₂		Ester	102
Ethyl propanoate	EP	C ₅ H ₁₀ O ₂		Ester	102
Propyl acetate	PA	C ₅ H ₁₀ O ₂		Ester	102
<i>iso</i> -Propyl acetate	IPA	C ₅ H ₁₀ O ₂		Ester	102
<i>n</i> -Butyl methyl ether	NBME	C ₅ H ₁₂ O		Ether	88
<i>sec</i> -Butyl methyl ether	SBME	C ₅ H ₁₀ O		Ether	88
Methyl <i>tert</i> -butyl ether	MTBE	C ₅ H ₁₀ O		Ether	88
Ethyl <i>tert</i> -butyl ether	ETBE	C ₆ H ₁₄ O		Ether	102
<i>tert</i> -Amyl methyl ether	TAME	C ₆ H ₁₄ O		Ether	102

of aromatic species in the undoped methane flames that serve as reference flames. To limit the effect of those uncertainties, the maximum mass of carbon in aromatics in each experiment is rescaled so that each undoped flame produces the same amount of soot precursors. This normalization step obviously

introduces some incertitude in the correlation procedure, which should be kept in mind in comparing the results of this analysis with those of the previous databases. The molecules used in the series of experiments are presented in Table 9. They include linear and branched alkanes, alcohol, ether, and ester

Table 10

Structure, occurrences, and contribution of the groups in Pfefferle et al.'s [18–20] study of CH₄ diffusion flames

Group	ID	Type	Occurrences	Contribution
CH ₄	2	Base fuel	17	0.004512
C-(C)(H) ₃	3	End	42	0.014381
C-(O)(H) ₃				
C-(CO)(H) ₃				
O-(C)(H)	4	End	4	-0.154549
C-(C) ₂ (H) ₂	6	Mid	19	0.107717
C-(C)(O)(H) ₂				
C-(C)(CO)(H) ₂				
O-(C) ₂	10	Mid	5	-0.099775
COO-(C) ₂	12	Mid	5	-0.087588
C-(C) ₃ (H)	14	Mid	6	0.334543
C-(C) ₂ (O)(H)				
C-(C) ₂ (CO)(H)				
C-(C) ₃ (O)	15	Mid	4	0.534714

molecules. The groups used in the analysis are similar to those used above and are described in Table 10. The modeling assumption is written as

$$\tilde{M}_{C,Ar} = \sum_{i=1}^{n_S} X_i \left(\sum_{j=1}^{n_{G,i}} N_{j,i} C_j^{M_{C,Ar}} \right), \quad (9)$$

where $\tilde{M}_{C,Ar}$ is the estimated maximum mass of carbon in aromatic species, X_i is the mole fraction of species i , and $C_j^{M_{C,Ar}}$ is the contribution of group j to $M_{C,Ar}$. The resulting correlation is displayed in Fig. 6 and group contributions are shown in Table 10. The correlation parameter is nearly 99%, the maximum error is 3.1%, and the average error is less than 2%. Hence, also for this set of experimental measurements, describing the data with the structural contributions of the fuel is shown to be a valid hypothesis. All oxygenated groups have a beneficial influence on (i.e., a negative contribution to) the amount of aromatic species produced. This means that the overall increase in aromatic concentration in the doped flames is clearly due to the hydrocarbon part of the additives. Also, the analysis once again points out that the more branched a molecule is, the higher the sooting tendency is, as both groups C-(C)₂(X)(H) (#14) and C-(C)₃(O) (#15) have a large positive coefficient.

The comparison between straight alkanes and oxygenates is also conducted for this database. The comparison is done for a constant carbon flux and a constant inert gas flow rate. Oxygenates are added so that the oxygen flux is 1% of the carbon flux. Then the same flow rate, that is, the same mole fraction of oxygenates, is replaced by pentane. The amount

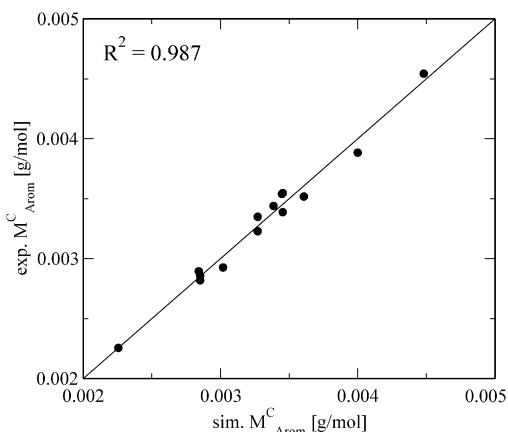


Fig. 6. Correlation between experimental and simulated carbon mass in aromatic species in Pfefferle et al.'s [18–20] study of CH₄ diffusion flames.

Table 11

Relative efficiency of oxygenated additives compared to pentane in Pfefferle et al.'s [18–20] study of CH₄ diffusion flames

Additive	Formula	Q_{CH_4} [cc/min]	Q_A [cc/min]	Improvement
Butanol	C ₄ H ₁₀ O	316.8	3.3	-20.72%
Methoxy-propane	C ₄ H ₁₀ O	316.8	3.3	-27.17%
Methyl butanoate	C ₅ H ₁₀ O ₂	321.75	1.65	-16.13%

of aromatics obtained when using the oxygenates is compared to the case when pentane is added. Results are presented in Table 11. For a constant oxygen flux, compared to pentane, ether shows a larger improvement than alcohol, which itself is more efficient than ester. This confirms the lower efficiency of esters compared to other oxygenated species, which was found in the analysis of the smoke point database and the homogeneous reactor simulation database.

5. Conclusion

A statistical method has been used to analyze several experimental databases. These databases included smoke point measurements of a large number of *n*-heptane/toluene/oxygenate mixtures obtained as part of this work, soot precursor concentrations in oxygenate-doped methane diffusion flames, and soot precursor levels obtained from simulations of rich premixed homogeneous reactors. The structure of the oxygenated molecules have been correlated with their sooting tendency with good accuracy. Two effects have been identified and quantified: the effect of the

oxygen moieties contained in the molecules, and the dilution effect, which replaces highly sooting components of the base fuel with cleaner hydrocarbons, or inversely, replaces clean-burning fuel with some more complex and sooting molecules. This dilution effect explained the seemingly contradictory observation that adding oxygenates to a methane diffusion flame actually increases the level of soot precursors in the flame. Overall, all oxygenated groups were found to reduce the sooting tendency of the base fuel to an extent that was shown to depend strongly on the nature of these groups. These conclusions have been reached using primarily large oxygenated molecules on specific sets of experimental data, and should not be generalized more than the original experiments would allow. For example, they may not be applicable to two studies by McEnally and Pfefferle [46] and McNesby et al. [47], which considered mixtures of ethylene and small oxygenated molecules such as ethanol and dimethyl ether, which both showed an increased sooting tendency when the oxygenate was added to the fuel. Further analysis involving detailed chemical arguments are warranted for these cases.

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