

Sooting characteristics of polyoxymethylene dimethyl ether blends with diesel in a diffusion flame

Yong Ren Tan¹, Maria L. Botero¹, Yuan Sheng², Jochen A.H. Dreyer³,
Rong Xu², Wenming Yang¹, Markus Kraft^{2,3}

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¹ Department of Mechanical Engineering
National University of Singapore
9 Engineering Drive
117575, Singapore

² School of Chemical and
Biomedical Engineering
Nanyang Technological University
62 Nanyang Drive
637459, Singapore

³ Department of Chemical Engineering
and Biotechnology
University of Cambridge
West Cambridge Site
Philippa Fawcett Drive
Cambridge CB3 0AS
United Kingdom
E-mail: mk306@cam.ac.uk

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Edited by

Computational Modelling Group
Department of Chemical Engineering and Biotechnology
University of Cambridge
West Cambridge Site
Philippa Fawcett Drive
Cambridge CB3 0AS
United Kingdom

Fax: + 44 (0)1223 334796

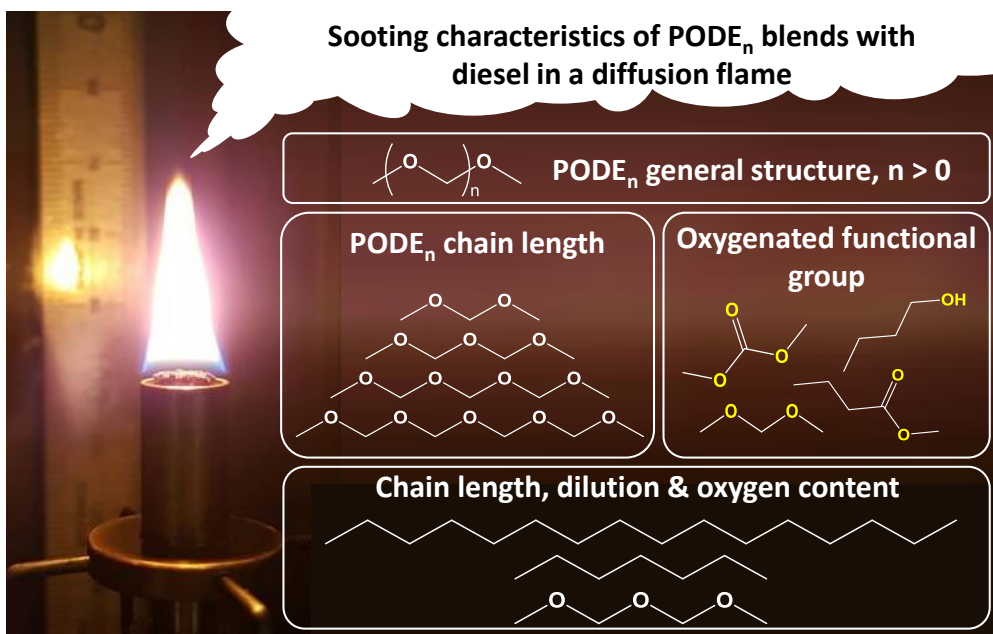
E-Mail: c4e@cam.ac.uk

World Wide Web: <http://como.cheng.cam.ac.uk/>



Abstract

In this paper, we investigate the sooting propensity of PODE_n/diesel blends. The sooting characteristics of PODE_n/diesel blends are determined using a standard ASTM D1322 smoke point lamp. The performance of PODE_n with different chain length (addition of -CH₂O- units) is benchmarked against other oxygenated soot suppression additives, including esters (methyl butyrate), carbonates (dimethyl carbonate) and alcohols (*n*-butanol). Soot reduction induced by the dilution of the aromatic fraction in the diesel fuel was found to have the biggest impact, followed by soot reduction by decreasing the hydrocarbon chain length and to a lesser extent increasing the oxygen content. The reason for the limited influence of oxygen content on soot suppression was further explored by examining the possible decomposition pathways and products of the different additives.



Highlights:

- The smoke points of diesel blends with PODE_n and several other oxygenated hydrocarbon additives were measured with a diffusion flame.
- Sooting propensity of all the oxygenated blends exhibited similar results.
- Oxygen content effect was found to have limited impact in comparison to dilution effect for soot suppression.

1 Introduction

Soot emitted due to incomplete combustion of hydrocarbon fuels is a major contributor to anthropogenic climate change and degrades air quality [1, 2]. Diesel combustion is among the major sources of soot emission, requiring the development of new additives and the formulation of cleaner diesel fuel mixtures. Oxygenated hydrocarbons are an example of such additives and their addition to diesel was shown to reduce soot emissions [3–5]. The most studied oxygenate additives for soot reduction are alcohols [6], ethers [7, 8], esters [9] and carbonates [8]. In the literature, it is reported that the soot-suppression efficiency of oxygenated hydrocarbons depends on the structure of the oxygenated species [10]. Alcohols and ethers are more effective than esters with the same mole fraction of oxygen in the fuel mixture. The reason is that the oxygen initially present in esters has CO₂ moieties which result in the direct production of CO₂ instead of oxygen radicals that promote the oxidation of soot or soot precursors [10]. In addition, dilution effects (replacement of highly sooting diesel by less sooting additives) contribute to the reduction of soot. Therefore, dilution should also be considered and distinguished from the chemical effect (presence of oxygen atoms in the additives) when evaluating the sooting propensity of fuel mixtures [11].

One of the most promising oxygenated fuel additives are poly(oxymethylene) dimethyl ethers (PODE) because of their ability to reduce soot without increasing the formation of other pollutants such as NO_x, CO or unburnt hydrocarbons [12, 13]. Furthermore, PODE can be produced on a large scale at prices compatible with conventional diesel [14–16]. In the past few years, several studies proved the suitability of PODE as an additive for gasoline and diesel in different engine configurations and its potential to achieve clean combustion [12, 13, 17–22].

PODE are polyether compounds with the general molecular structure CH₃O(CH₂O)_nCH₃ ($n > 0$), as shown in Fig. 1. Abbreviations used in literature for PODE_n are POMDME_n, PODE_n, DMM_n or OME_n. The physical properties of PODE_n have been studied extensively [23, 24]. They have a high cetane number [25], high oxygen content and are free of sulfur and aromatics which make them an ideal candidate as fuel additive. However, PODE_n with $n < 2$ has a too low flash point while the high viscosity and cloud point for $n > 5$ does not comply with the regulations for fuels used in engines [15, 26]. Therefore, the optimal chain length for PODE_n is $n = 3-4$ [14].

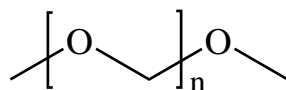


Figure 1: Molecular structure of PODE_n series where $n > 0$.

In spite of the great potential of PODE as fuel additive, there are only few studies focusing on the fundamental understanding of its role in soot suppression. In a kinetic study, Sun et al. [27] concluded that the soot-reduction potential was due to the absence of C-C bonds in PODE. However, the influence of the individual polyether compounds present in PODE on its sooting propensity, as well as the effect of chain length, is still unknown.

The purpose of this study is to elucidate the influence of PODE_n ($n = 1,2,3,4$) chain length

on the sooting propensity of PODE_{*n*}-diesel blends. The smoke point (SP) is used as a standardised method (ASTM D1322) [28] to quantify the sooting propensity of the liquid fuels. Furthermore, the Threshold Sooting Index (TSI) and Oxygenated Extended Sooting Index (OESI) are calculated because their linear relationship to fuel composition facilitates the analysis of fuel mixtures [29, 30]. A comparison of the soot suppression ability with respect to other prospective oxygenated fuel additives, *i.e.* methyl butyrate (MB), dimethyl carbonate (DMC) and *n*-butanol (BuOH) is also presented in an effort to illustrate a more comprehensive discussion of sooting propensities among oxygenates.

2 Materials and methods

2.1 Methodology

A standard ASTM D1322 [28] smoke point lamp burner (Koehler Instrument Company, Inc., Bohemia, NY) was used to generate the non-premixed diffusion flame and to measure the smoke point (SP) of the fuel blends. The SP burner consists of a cylindrical reservoir, with an inner concentric hole to place the wick. The exterior of the burner tube was adapted with a light weight Delrin™ fitting with four brass struts that connect to the wick sheath [31]. Thus, the wick exposure and the flame height can be adjusted by rotating the threaded fitting, as described previously [31–33]. The wick height has been increased from 6 mm to 12 mm to achieve greater flame heights, up to 80 mm.

The SP of a fuel is defined as the maximum flame height (in mm) produced in the SP lamp without smoke leaving the flame. The higher the SP, the lower the sooting tendency of the fuel tested. The SP lamp has been calibrated using 20 vol.% toluene-80 vol.% iso-octane and 40 vol.% toluene-60 vol.% iso-octane, as specified in ASTM D1322 [28]. Each fuel blend was then tested five times in order to obtain an average smoke point and error estimate.

An empirical correlation known as Threshold Sooting Index (TSI) has been proposed by Calcote and Manos [34] that is proportional to the sooting tendency and that enables the comparison between different SP apparatus. As shown in Eq. (1), the TSI is directly proportional to the ratio of the molecular weight (MW) to the SP. The coefficients a_{TSI} and b_{TSI} are constants which are dependent on the utilised SP lamp.

$$TSI = a_{\text{TSI}} \left(\frac{MW}{SP} \right) + b_{\text{TSI}} \quad (1)$$

The MW was included to account for the higher oxygen requirement for stoichiometric combustion as the MW in the fuel increases, which has an increase in the flame height. However, this approximation is not suitable for oxygenated fuels, because it fails to account for the oxygen provided by the fuel, as acknowledged by Calcote and Manos [34]. Barrientos et al. [35] proposed a modification to the TSI, known as Oxygen Extended Sooting Index (OESI). The OESI accounts for oxygen in the fuel by replacing MW in Eq. (1) with $(n + \frac{m}{4} - \frac{p}{2})$, as shown in Eq. (2). Hereby, *n*, *m* and *p*, are the coefficients of carbon, hydrogen and oxygen of a generic fuel C_{*n*}H_{*m*}O_{*p*}. Consequently, the OESI ac-

counts for a reduced oxygen requirement from the surrounding air for a stoichiometric combustion in the case of oxygenated fuels [35]. The constants a_{OESI} and b_{OESI} are dependent on the SP lamp used.

$$\text{OESI} = a_{\text{OESI}} \left(\frac{n + \frac{m}{4} - \frac{p}{2}}{\text{SP}} \right) + b_{\text{OESI}} \quad (2)$$

In order to compute the constants a and b of the TSI and OESI, *n*-heptane (HEP) and 1-methylnaphthalene (1-MN) were used. The TSI and OESI of HEP and 1-MN were set to 2.6 and 91, respectively, in accordance to the TSI values suggested by Olson et al. [36], which are widely used in literature [35, 37, 38]. The SP of pure HEP and 1-MN were measured to be 75 ± 5 mm [39] and 5 ± 1 mm, respectively. The derived TSI and OESI model constants are tabulated in Table 1. For non-oxygenated fuels, the TSI and OESI are assumed to be identical as $(n + \frac{m}{4} - \frac{p}{2})$ is almost proportional to MW [35]. The error was determined using the error propagation method published by Watson et al. [31].

Table 1: TSI and OESI constant determined from the SP of the reference compounds.

$\mathbf{a_{\text{TSI}}}$	$\mathbf{b_{\text{TSI}}}$	$\mathbf{a_{\text{OESI}}}$	$\mathbf{b_{\text{OESI}}}$
3.3 ± 0.3	-1.8 ± 0.3	34.6 ± 3.7	-2.5 ± 0.4

2.2 Fuels

The fuels studied in the current investigation and their physical properties are listed in Table 2. PODE₂, PODE₃ and PODE₄ were purchased from Beyond Industries (China) Limited with 96%, 97%, 97% purity, respectively. *n*-Hexadecane (HD), *n*-heptane (HEP), *n*-butanol (BuOH), dimethoxymethane (DMM or PODE₁), methyl butyrate (MB), and dimethyl carbonate (DMC) used in current investigation were purchased from Sigma-Aldrich with 99% purity. BuOH, MB and DMC were selected to compare the sooting propensity of additives with different oxygenated functional groups but similar chemical structure as PODE. A commercial diesel fuel was obtained from a petrol station in Singapore, and its chemical analysis is presented in Table 3.

3 Results and Discussion

The SP, TSI and OESI of the commercial diesel fuel, PODE₁, PODE₂, PODE₃, and PODE₄ are reported in Table 4. Measuring the SP of the pure PODE_{*n*} fuels was not possible as the flame was non-luminous and the soot breakthrough point of the flame could not be reached. Therefore, the values for the oxygenated fuels are estimated from the extrapolation of the PODE_{*n*}/diesel blends, in accordance to the TSI mixing rule [29]. The SP of PODE₄ blends were measured only up to 30 vol.% due to its immiscibility at higher concentrations.

Table 2: *Physical properties of commercial diesel fuel and PODE_n series.*

Properties	Method	Diesel fuel	PODE ₁	PODE ₂	PODE ₃	PODE ₄
Molecular formula		C _{16.8} H _{28.6} ¹	C ₃ H ₈ O ₂	C ₄ H ₁₀ O ₃	C ₅ H ₁₂ O ₄	C ₆ H ₁₄ O ₅
Density at 20°C (kg/m ³)	Pycnometry	0.84	0.86	0.97	1.02	1.07
Oxygen content (wt.%)		0	42	45	47	48
Molecular weight (g/mol)		237.98 ²	76.09	106.12	136.14	166.17
Distillation temperature	ASTM D86-16a					
IBP ⁴ (°C)		194.0	-	-	-	-
10% recovered (°C)		223.6	-	-	-	-
50% recovered (°C)		294.4	-	-	-	-
90% recovered (°C)		356.7	-	-	-	-
FBP ⁴ (°C)		375.6	42 ³	105 ³	156 ³	202 ³

¹ The molecular formula of diesel is derived from the data collected from elementary analysis (CHNS).

² Averaged MW determined from Aspen Tech Hysys software using ASTM D86-16a and density data.

³ PODE_n FBP is obtained from Ref. [25].

⁴ IBP = Initial boiling point; FBP= Final boiling point

Table 3: *Composition of commercial diesel fuel.*

Composition	Method	Percentage(%)
Types of hydrocarbon	GC/MS ¹	
Straight-chain alkanes		16.33
Branched alkanes		21.46
Cyclo-alkanes		4.62
Alkenes		3.57
Aromatics		9.00
Alkane (Unidentified)		21.85
Aromatic (Unidentified)		23.17
Elements	Elementary Analysis (CHNS) ²	
Carbon (wt.)		88.31
Hydrogen (wt.)		11.69
Nitrogen (wt.)		0
Sulfur (wt.)		0

¹ Agilent 7890 GC / 5975 MSD with HP-5ms column was used. Method: Starting temperature at 80 °C and hold for 10 minutes. Then, ramp up to 280 °C with 1 °C/min and hold for 35 minutes.

² Elementary analysis (CHNS) has been performed using Elementar vario MICRO cube.

Table 4: *SP, TSI, and OESI for the pure diesel and oxygenated fuels.*

Properties	Method	Diesel fuel	PODE ₁	PODE ₂	PODE ₃	PODE ₄
SP (mm)	ASTM D1322	14.8	-	-	-	-
TSI	-	51.3	2.6 ¹	0.2 ¹	0.9 ¹	8.6 ¹
OESI	-	53.7	-2.5 ¹	-7.4 ¹	-8.7 ¹	-8.8 ¹

¹ Estimated value from extrapolation of TSI and OESI for oxygenates/diesel blend.

3.1 Sooting indices and dilution effect

The TSI and OESI are proportional to the sooting propensity. A decrease in these indices corresponds to a decreased sooting tendency of the fuels. The TSI and OESI of oxygenated hydrocarbon (PODE₂) and non-oxygenated hydrocarbon (HEP and HD) blends with diesel versus their mole fraction are shown in Fig. 2. The addition of the fuels to diesel decreases the sooting tendencies linearly. Notably, the uncertainty of the TSI and OESI decreases with increasing the additive mole fraction, as seen by the decreasing error bars. A similar trend was reported by Watson et al. [31] and explained by the higher deviation in measuring the flame height at low SPs.

As seen in Fig. 2a, the TSI of diesel blends with HD is higher than that with HEP and PODE₂, which is not surprising given the higher soot propensity of long-chained hydrocarbons. In contrast, the TSI of the fuel mixture with HEP and PODE₂ are almost identical, indicating a similar degree of soot reduction ability. The similarity between oxygenated and non-oxygenated fuel additives does not reflect the expected trend reported in literature [11]. However, when using the OESI (Fig. 2b), the differences between HEP and PODE₂ increase at mole fractions above 0.4. Therefore, the OESI appears to be better suited for comparing oxygenated and non-oxygenated fuels.

The chemical analysis (see Tables 2 and 3) indicates that the utilised diesel mainly consists of alkanes with an average of about 16 carbon atoms. Therefore, the addition of the straight-chained alkane HD (C₁₆H₃₄) to diesel solely reduces the percentage of more sooty aromatic hydrocarbons in diesel [40, 41], giving insight into the dilution effect [11]. Fig. 3 presents the OESI of PODE₂, HEP and HD blends with diesel versus their volumetric fraction in the mixture. It can be seen that diesel dilution with HD leads to a substantial reduction of the OESI (46% for a 50 vol.% blend). The addition of HEP also dilutes the diesel fuel but additionally decreases the average chain length of the blend, resulting in a further decrease of the OESI (overall 71% at 50 vol.%; see Fig. 3). In comparison, a 50 vol.% diesel/PODE₂ blend reduces the OESI by an additional 16% (overall 86% at 50 vol.%), attributed to a combined dilution, hydrocarbon chain length reduction and oxygen content effect. In the further evaluation of soot suppression ability of oxygenated fuels, the combination of these three effects will be taken into account.

3.2 PODE chain length effect

A series of PODE_{*n*} was studied as it permits a systematic increase in the oxygen content within the molecule without adding C-C bonds. Also, PODE_{*n*} are straight chained

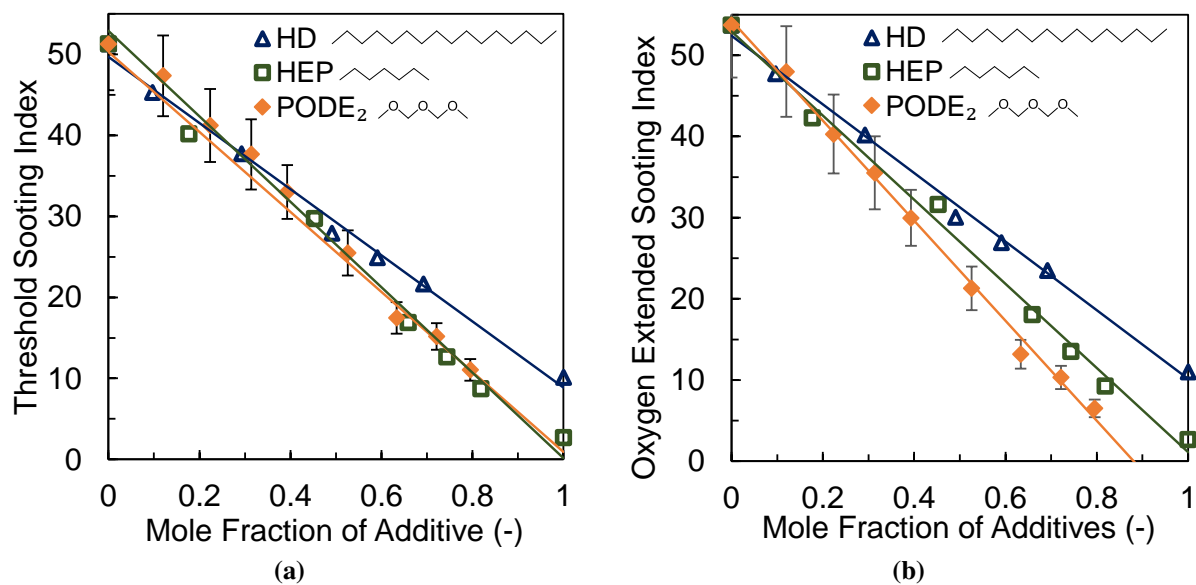


Figure 2: (a) TSI and (b) OESI values versus mole fraction of PODE₂, HEP, and HD - with diesel. Error bars for PODE₂-diesel blends are shown as an example. Correlation coefficient (R^2) for all linear regression are > 0.99 .

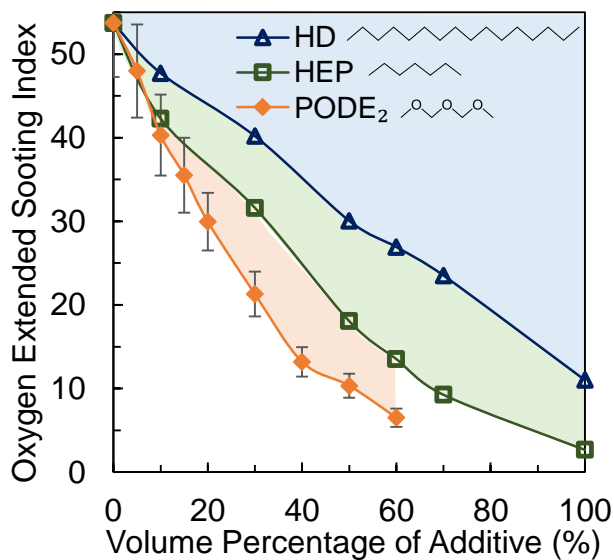


Figure 3: OESI values versus additive volume percentage of PODE₂, HEP, and HD in diesel. Error bars for the PODE₂-diesel blend are shown as an example. The color shaded region represents: Dilution effect, Hydrocarbon chain length reduction effect, Oxygen content effect.

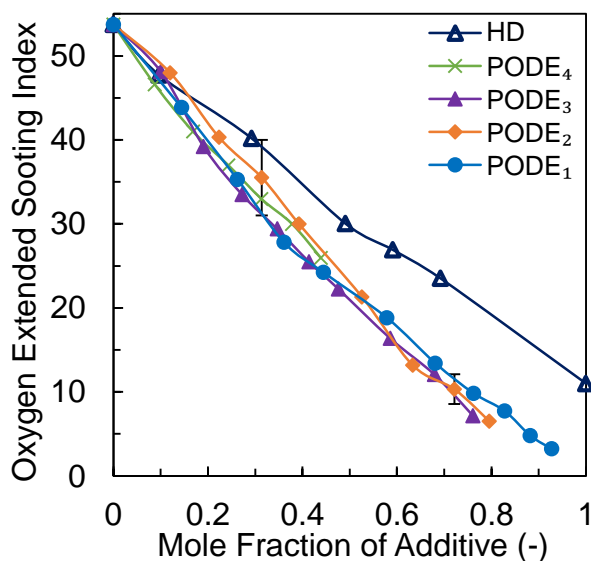


Figure 4: OESI value versus the mole fraction of the PODE_n additive in diesel. HD/diesel blends are included to indicate the extent of OESI reduction due to dilution. Error bars for the PODE₂-diesel blend are shown as an example.

molecules and as such, are expected to possess a low sooting propensity [42].

In Fig. 4 the OESI of the PODE_n blends are plotted against the mole fraction of the fuel additives. All the PODE_n decrease the sooting tendency of the fuel mixture with increasing its mole fraction. The difference in soot reduction with increasing PODE_n chain length is negligible and within the margin of error. This indicates that at the same mole fraction, increasing the oxygen content in PODE_n by adding -CH₂O- subunits has little influence on the soot reduction.

As fuels are commonly blended by volume percent in engine applications, Fig. 5 presents the OESI versus volume percentage of HD and PODE_n in the blend with diesel. Similar to the additive mole fraction, an increase in the PODE_n volume percentage leads to a decrease in the sooting tendency. In the range of 5 vol.% to 30 vol.% PODE_n, PODE₁ appears to possess a slightly better soot reduction ability than PODE₂-PODE₄. However, substantial experimental error at small SP and thus high OESI prevents an unambiguous conclusion. It is worth noting that the oxygen addition by introducing PODE_n only accounts for 14-20% OESI decrease while the 44-72% decrease can be traced to the dilution effect (see HD in Fig. 5).

Fig. 4 and 5 indicate that an increase in oxygen content in the fuel additive *via* PODE_n chain length increase has a negligible effect on the sooting propensity of the fuel mixtures. However, the oxygen content in the fuel blend is different for each PODE_n at the same mole or volume fraction added to diesel. Therefore, the OESI was plotted over the oxygen content in the fuel blend in Fig. 6. Interestingly, at a given oxygen content in the blend, the OESI seems to decrease with decreasing PODE_n chain length. This becomes especially evident in the region of 10-20 wt.% oxygen fraction, while the OESI converges towards similar values at higher oxygen concentrations.

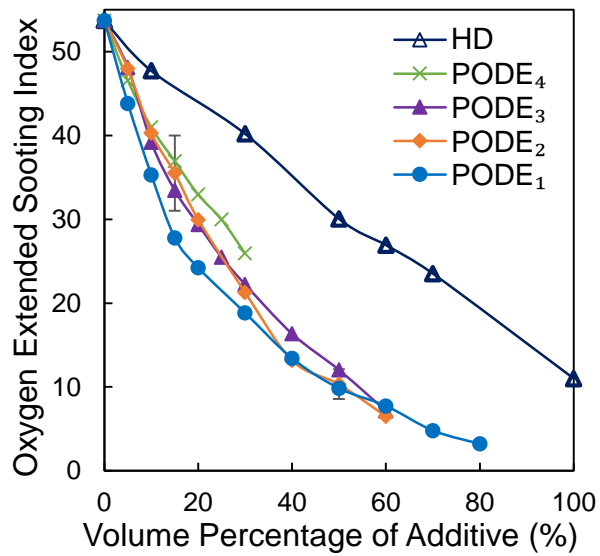


Figure 5: OESI versus the volume percentage of $PODE_n$ additive in diesel. HD/diesel blends are included to indicate the extent of OESI reduction due to dilution. Error bars for the $PODE_2$ -diesel blend are shown as an example.

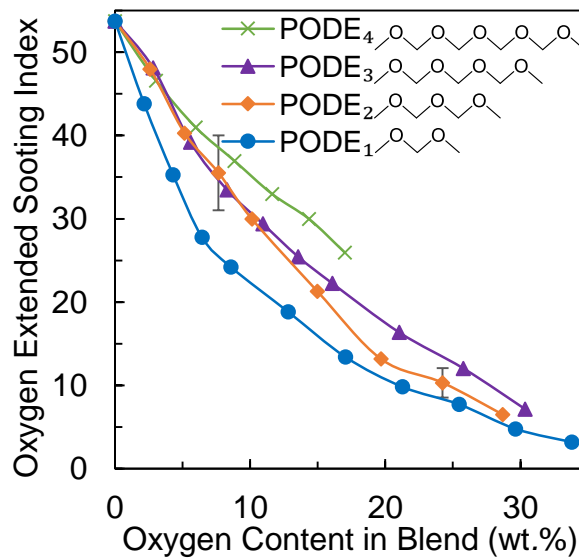
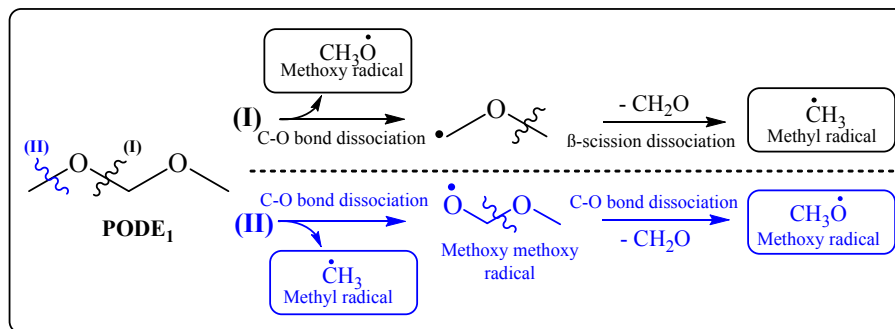
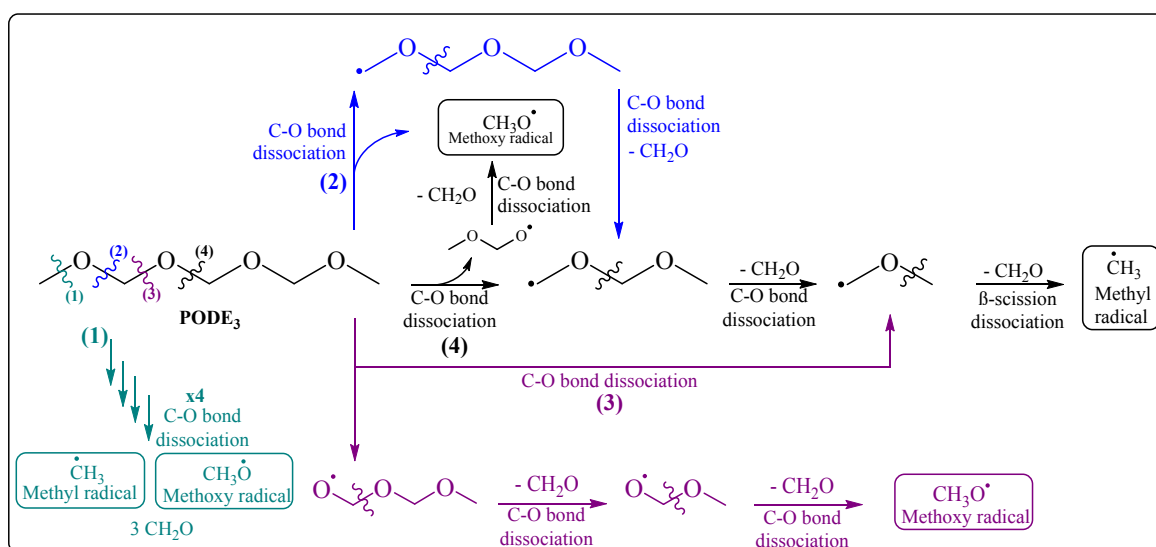


Figure 6: OESI versus the oxygen content in fuel blends of the $PODE_n$ with diesel.



(a)



(b)

Figure 7: Proposed reaction pathways, reaction intermediates, and products species for (a) PODE_1 and (b) PODE_3 decomposition.

The effect of chain length in PODE_n can be rationalised from the possible decomposition mechanisms based on the reaction pathways suggested by McEnally and Pfefferle [42] for straight ether compounds in non-premixed flames. More mechanisms involving PODE_1 and ethers in non-premixed flames and flow reactors can be found in literature [27, 43–45].

In pathway (I), PODE_1 dissociates *via* a two-step reaction: C-O bond dissociation followed by β -scission dissociation reactions (Fig. 7a). Alternatively, PODE_1 can undergo two consecutive C-O bond dissociations *via* path (II) (Fig. 7a). The PODE_n series is postulated to follow similar decomposition pathways [42] as exemplified for PODE_3 in Fig. 7b. More generally, the amount of released formaldehyde (CH_2O) increases proportionally with increasing chain length, whilst the amount of methoxy radicals and methyl radicals remains constant. In a kinetic study, Sun et al. [27] reported that an increase in the PODE_n chain length increased the production of CH_2O and lowered formation of $\text{CH}_3\cdot$ radicals. Thus, hydrocarbons that are larger than C_2 are rarely formed and the general formula for PODE_n decomposition can be written as shown in Fig. 8.

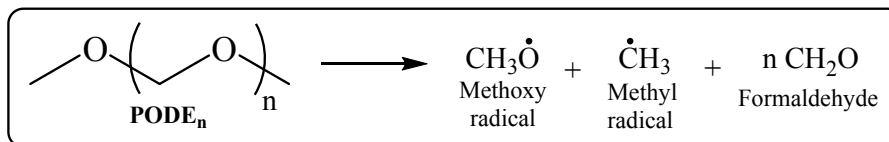


Figure 8: General formula for the decomposition of PODE_n during combustion in non-premixed flames.

The general PODE_n decomposition mechanism in Fig. 8 suggests three main products: methoxy radical ($\text{CH}_3\dot{\text{O}}$), methyl radical ($\dot{\text{C}}\text{H}_3$), and formaldehyde (CH_2O). Oxygen in the form of CH_2O is less efficient in suppressing soot as it is easily converted to carbon monoxide without participating in the oxidation of soot precursors [46]. In contrast, oxygen in $\text{CH}_3\dot{\text{O}}$ radicals can be converted through thermal decomposition or react with molecular oxygen to produce oxidising species (O^\bullet , HO^\bullet , HO_2^\bullet , H^\bullet) [46–49]. Thus, increasing the chain length of PODE_n does not increase the amount of species able to suppress soot but only CH_2O .

This explains the trend of a lower soot suppression (*i.e.*, lower OESI) at a given oxygen fraction with increasing PODE_n size (Fig. 6). It should be noted that the decomposition pathways proposed in Fig. 7 are not exhaustive. A detailed experimental investigation of a non-premixed flame, focusing on the decomposition kinetics and pathways of PODE_n would be required, which is beyond the scope of this work.

3.3 Comparison with other oxygenated fuels

Additional experiments were conducted with *n*-butanol (BuOH), methyl butyrate (MB), and dimethyl carbonate (DMC) to elucidate the effect of functional groups and oxygen moieties on soot suppression. They are representatives of esters (MB), carbonates (DMC) and alcohols (BuOH), which were shown to be potential candidates as fuel additives in diesel engines [10]. Besides, they have been previously studied in non-premixed flames and their thermal decomposition pathways were reported in literature [50–53]. These three additives were benchmarked against PODE_1 and PODE_2 due to their comparable molecular size.

Fig. 9 presents the calculated OESI for the different oxygenated fuel blends with diesel as a function of their mole fraction (Fig. 9a) and volume percentage (Fig. 9b). All the oxygenated fuels show similar propensity for soot reduction within the margin of error. Oxygen content in the fuels induces an additional 18–26% of soot reduction, while the remaining is attributed to the dilution effect (44–72%). Fig. 9b also suggests that in engine applications where volumetric blends are used, there is no clear benefit in using one oxygenate for soot reduction over another.

In Fig. 10, the OESI is plotted against the oxygen content in the fuel blend. Here, BuOH shows the greatest reduction of soot at the same oxygen content among the tested oxygenated fuel additives. The order of soot suppression observed is: $\text{BuOH} > \text{MB} > \text{PODE}_1 > \text{PODE}_2 \approx \text{DMC}$. The results and trends agree with previous studies [37, 52] and indicate that the oxygen content of the molecule is not the sole contributing factor to soot

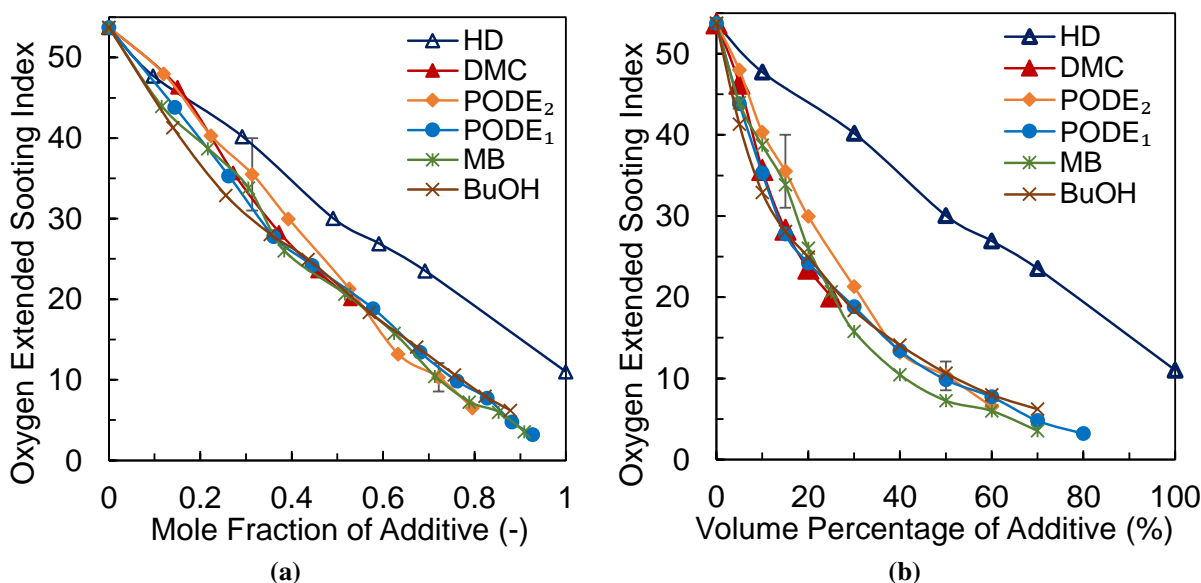


Figure 9: OESI value versus (a) the mole fraction and (b) the volume percentage of the oxygenated additives in diesel.

reduction. It is also in-line with the conclusion by Pepiot-Desjardins where aldehydes or long-chain alcohols appeared to be the most effective soot reducers compared to other types of functional groups such as esters or ethers [10, 11]. Understanding the role of the oxygen moiety of the different additives requires a closer look at their decomposition pathways and potential reaction products.

The possible decomposition pathways of BuOH are depicted in Fig. 11 [50]. The most significant pathway (1) is the simple fission, with initial C-C bond dissociation to produce alkyl radicals and hydroxyalkyl radicals. The alkyl radical then dissociates by β -scission to alkenes and aldehydes. The C-C bond adjacent to the hydroxyl group is weaker, thus it is more susceptible to dissociation [50]. The H-abstraction decomposition pathway (2) may also play a significant role in soot reduction as it produces active hydroxyl radicals (HO^\bullet), which are known to reduce soot [48, 49, 54]. This is in agreement with a computational study of butanol/benzene flames which explained the ability of BuOH to suppress soot by an increased number of radicals that favour the consumption of the soot precursor propargyl radical ($\text{C}_3\text{H}_3^\bullet$) [55].

In MB pyrolysis, some notable decomposition products are carbon dioxide (CO_2) and methoxy radicals [10, 52]. Oxygen in CO_2 is not available for the oxidation of soot precursors which explains why MB is less effective in soot suppression than BuOH. The formed methoxy ($\text{CH}_3\text{O}^\bullet$) radicals contribute to soot suppression but not as strongly as OH^\bullet radicals formed during BuOH decomposition [10]. Meanwhile, DMC most likely decompose through C-O bond dissociation forming a methyl radical and a carbonate radical (Fig. 12). The carbonate radical can dissociate through β -scission to form a $\text{CH}_3\text{O}^\bullet$ radicals and CO_2 [51]. The sooting tendency of DMC and PODE_2 are similar because only one of their three oxygen atoms is available for the $\text{CH}_3\text{O}^\bullet$ radical production, which has soot suppression ability. The other two oxygen in DMC may not be fully utilized for

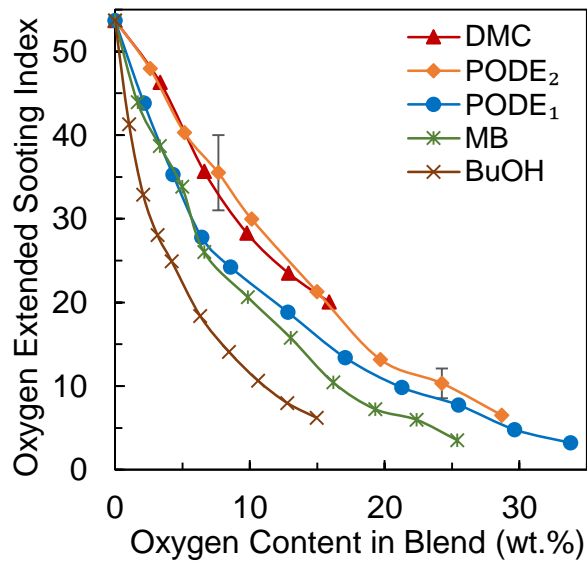


Figure 10: OESI versus oxygen content in the blends of oxygenated additives with diesel.

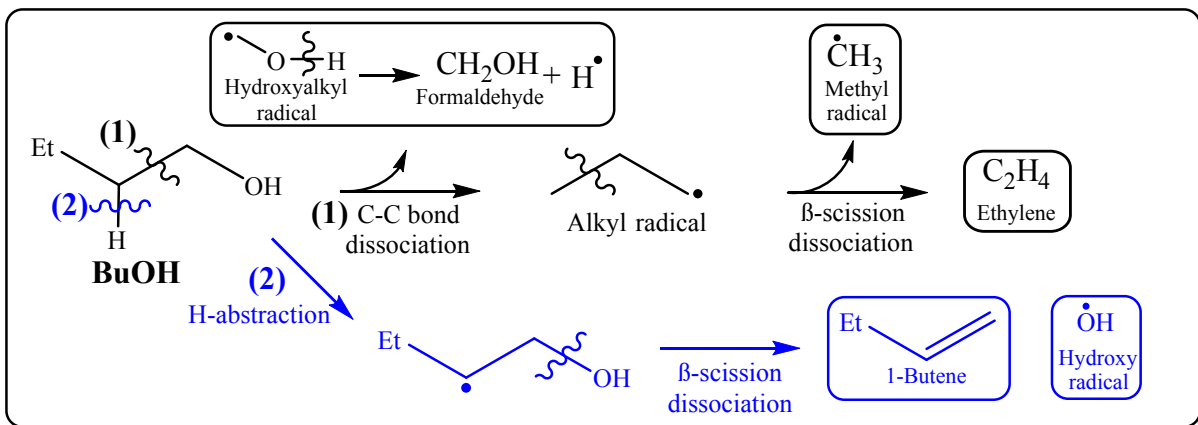


Figure 11: Proposed dominant decomposition pathways of BuOH.

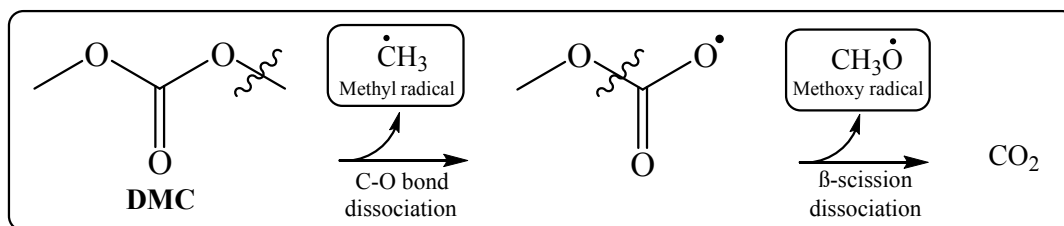


Figure 12: Proposed dominant decomposition pathway of DMC.

soot suppression, as explained previously for PODE_{*n*}.

In the current investigation, the soot reduction abilities of oxygenated additives have mainly been rationalised by simple decomposition pathway arguments and the identification of ‘active’ oxygenated soot-reducing moieties. Nevertheless, the observed trends were well explained by these simple considerations and might set the foundation for future design of soot reduction additives by maximising the chemical effect of the oxygenated molecules (*i.e.*, increase number of ‘active’ soot suppression species).

4 Conclusions

The sooting propensities of PODE_{*n*}, BuOH, DMC and MB blends with commercial diesel fuel were investigated using the smoke point ASTM D1322 method. The fuel dilution and chemical effect (chain length and oxygen content) of the additives were studied as well as the effect of PODE_{*n*} chain length. The influence of the type of oxygenated functional groups on the sooting propensity of the fuel blends was also explored. The conclusions of this investigation are summarised as follows:

- **Dilution and oxygen content effects.** In all the oxygenated blends, the dilution of the aromatics in diesel accounts for the majority of the soot reduction, namely 44-72%. The oxygen content of the fuels contributes less to the soot reduction, between 18-26%. This has an important implication for engine applications as in terms of volumetric addition of oxygenates, there is no noticeable difference in using one oxygenated additive or another.
- **Chain length effect.** In the PODE_{*n*} series, there was no clear differences in the soot suppression ability of the additives at the same mole fraction or volume percent. However, when comparing the oxygen content of the additive-diesel blends, the soot suppression ability of the PODE_{*n*} has the trend of PODE₁ > PODE₂ > PODE₃ > PODE₄. The increase in PODE_{*n*} chain length does not increase the soot reduction ability as the additional oxygen may not be actively involved in soot suppression. Thus, the oxygen content in the oxygenated additives is not the sole factor in defining the sooting reduction, the decomposition pathways and the identification of ‘active’ oxygenated soot-reducing moieties play a more crucial role.
- **Oxygenated functional group effect.** PODE₁ and PODE₂ were compared to other hydrocarbons with different oxygenated functional groups. The soot suppression

ability followed the trend: BuOH > MB > POE₁ > POE₂ ≈ DMC. Despite having only 22 wt.% of oxygen, BuOH showed a superior soot suppression ability due to the presence of the alcohol functional group, which facilitates OH• radical formation, a strong soot suppression species. The other oxygenated additives can produce CH₃O• radicals that could act as soot suppression species and their performance can be rated by their efficiency to utilize their oxygen for the OH• radical production.

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