Full Length Article

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

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GRAPHICAL ABSTRACT
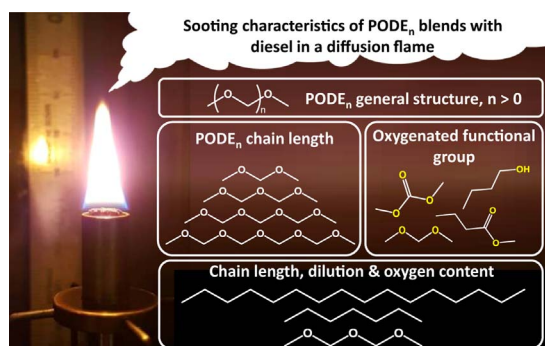
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ABSTRACT

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 ASTMD1322 smoke point lamp. The performance of $PODE_n$ with different chain length (addition of $-CH_2O-$ 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.

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 [3–7]. The most studied oxygenate additives for soot reduction are alcohols [8], ethers [9,10], esters [11] and carbonates [10]. In the literature, it has been reported that the soot-suppression efficiency of oxygenated hydrocarbons is influenced solely by

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the oxygen content in the oxygenated fuel [4,12]. Conversely, other studies have shown that the soot-suppression efficiency of oxygenated hydrocarbons also depends on the structure of the oxygenated species [13,14]. 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 CO_2 moieties which result in the direct production of CO_2 instead of oxygen radicals that promote the oxidation of soot or soot precursors [13]. 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 [15].

One of the most promising oxygenated fuel additives are poly (oxymethylene) dimethyl ethers (PODE). Recent studies have exalted, under some particular engine configuration and operation conditions, their ability to reduce soot without increasing the formation of other pollutants such as NO_x, CO or unburnt hydrocarbons [16,17]. 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 [16–23]. Furthermore, it can be produced on a large scale at prices compatible with conventional diesel [24–26].

PODE are polyether compounds with the general molecular structure $CH_3O(CH_2O)_nCH_3$ ($n > 0$), as shown in Fig. 1. Alternative 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 [27,28]. They have a high cetane number [29], 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 [25,30]. Therefore, the optimal chain length for $PODE_n$ is $n = 3–4$ [24].

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. [31] 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 (ASTMD1322) [32] 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 [33,34]. 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. Methods

A standard ASTMD1322 [32] 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
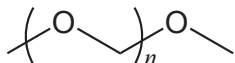
Fig. 1. Molecular structure of $PODE_n$ series where $n > 0$.

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 [35]. Thus, the wick exposure and the flame height can be adjusted by rotating the threaded fitting, as described previously [35–37]. 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 ASTMD1322 [32]. 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 [38] 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.

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

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 [38]. Barrientos et al. [39] 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 $\left(n + \frac{m}{4} - \frac{p}{2}\right)$, as shown in Eq. (2). Hereby, n, m and p, are the coefficients of carbon, hydrogen and oxygen of a generic fuel $C_nH_mO_p$. Consequently, the OESI accounts for a reduced oxygen requirement from the surrounding air for a stoichiometric combustion in the case of oxygenated fuels [39]. The constants a_{OESI} and b_{OESI} are dependent on the SP lamp used.

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

In order to compute the constants a and b of the TSI and OESI, n-heptane and 1-methylnapthalene (1-MN) were used. The TSI and OESI of heptane and 1-MN were set to 2.6 and 91, respectively, in accordance to the TSI values suggested by Olson et al. [40], which are widely used in literature [39,41,42]. The SP of pure heptane and 1-MN were measured to be 75 ± 5 mm [43] 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 $\left(n + \frac{m}{4} - \frac{p}{2}\right)$ is almost proportional to MW [39]. The error was determined using the error propagation method published by Watson et. al. [35].

2.2. Fuels

The fuels studied in the current investigation and their physical properties are listed in Table 2. $PODE_2$, $PODE_3$ and $PODE_4$ were purchased from Beyond Industries (China) Limited with 96%, 97%, 97% purity, respectively. n-Hexadecane, n-heptane, n-butanol (BuOH), dimethoxymethane (DMM or $PODE_1$), methyl butyrate (MB), and dimethyl carbonate (DMC) used in current investigation were purchased

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

a_{TSI}	b_{TSI}	a_{OESI}	b_{OESI}
3.3 ± 0.3	-1.8 ± 0.3	34.6 ± 3.7	-2.5 ± 0.4