

A CHEMICAL KINETIC MODELING STUDY OF THE EFFECTS OF OXYGENATED SPECIES ON SOOT EMISSIONS FROM DIESEL ENGINES

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ABSTRACT

The role of oxygenated hydrocarbons in reducing soot precursors from diesel engines is studied using a detailed chemical kinetic model. Since diesel is a complex mixture of several hundreds of hydrocarbons, it is represented by a surrogate made of n-dodecane and m-xylene, whose composition is defined to match the threshold sooting index of the real fuel. Two oxygenates, namely methanol and dimethyl ether are considered, owing to their relevance as alternative fuels. Our analysis reveals that oxygenates decrease the overall equivalence ratio of the mixture thus producing higher ignition temperatures and more radical species to consume more soot precursor species, leading to lower soot production. These observations, which are in line with current understanding of the action of oxygenates on reduction of soot, are exemplified by a fundamental path flux analysis of the production and consumption routes of acetylene, which is the dominant soot precursor in this case.

Keywords: soot, oxygenates, diesel

NOMENCLATURE

DME Dimethyl ether

INTRODUCTION

Emissions from automobiles, especially diesel engines, continue to be a serious environmental concern. Although a lot of work has been done on reducing emissions from diesel engines in the recent past, the emission norms have also been steadily tightened. To meet these strict regulations, fundamental knowledge about soot production is absolutely

necessary. Different hydrocarbon fuels can produce different amounts of soot and altering the fuel composition can help in reducing soot production [1]. Methanol and DME are being increasingly investigated as additives to diesel fuels for this purpose (for instance, Refs. [2]).

Methanol is a promising alternative fuel due to its advantages of low price and high oxygen fraction. It is considered CO₂-neutral with regard to the greenhouse effect because the same amounts of carbon dioxide (CO₂) and water (H₂O) that result from complete combustion are needed for the photosynthesis of plants from which they are produced. The global demand for methanol has increased steadily in recent decades because of its direct use as liquid fuel to power passenger cars and its role as feedstock for the production of DME, which is of interest as a potentially clean alternative to diesel fuel.

DME is a liquefied gas that can be produced from a variety of feed stock, is non-toxic and environmentally benign. DME's main feature as an efficient alternative fuel for use in compression-ignition engines is its high cetane number (>55). It is as easy to handle as LPG since it is condensed by pressurizing above 0.5 MPa. The fast evaporation of DME can lead to better mixing with air in the engine cylinder and its high oxygen content can achieve smokeless combustion through low formation and high oxidation rates of particulates.

Many previous studies have shown that addition of oxygenates to diesel fuel reduces the amount of soot produced [1, 3, 4]. Miyamoto *et al.* [4] performed experi-

ments and found that soot emissions from diesel engines were reduced when oxygenated hydrocarbons were blended with diesel fuel. Litzinger *et al.* [5] combined experimental and kinetic modeling analysis of the soot-reducing effects of oxygenated species (*i.e.*, ethanol and DME) on sooting laminar premixed and diffusion ethane-air and ethylene-air flames, and while these flames and fuel are quite distinct from diesel combustion, they provide valuable chemical insights into soot reduction chemistry.

The present work is a continuation of the previous work of Westbrook *et al.* [3]. In that study, detailed chemical kinetic modeling was used to study soot reduction in diesel engines by addition of oxygenates using *n*-heptane as a surrogate for diesel. In the present study, a similar analysis to that of Westbrook *et al.* [3] is performed, nonetheless, with a surrogate that is more representative of the sooting behaviour of the real diesel fuel. The objective of this study is to investigate (a) the importance of the fuel representation itself on the effectiveness of methanol and DME as additives to diesel fuel and (b) delineate the pathways producing and consuming soot precursors in the presence of these oxygenates quantitatively using a reaction path flux analysis.

MODELING APPROACH

The conceptual model for diesel combustion developed by Dec [6], describes the major chemical and physical steps that occur during diesel combustion. The important process which produces the soot precursor species is the fuel-rich premixed ignition, whose products cannot be oxidized completely, due to the absence of any more oxygen. These incompletely oxidized species such as CO, H₂ and small intermediate hydrocarbon species including acetylene, ethene, propene and others then react to produce soot. These small unsaturated hydrocarbon species have been identified as major contributors to soot production in diesel engines.

In this study, the rich, premixed diesel ignition is computed using a detailed chemical mechanism for the diesel fuel and the oxygenated species. The ignition calculation is carried out under conditions of pressure, temperature and fuel/air ratios that are characteristic of a diesel engine at the top of the piston stroke, as identified by Westbrook *et al.* [3].

To carry out these calculations, a surrogate approach is taken to represent the real diesel fuel. In the present study two different surrogates are considered for diesel fuel: (a) a mixture of 45% *n*-dodecane and 55% *m*-xylene (Surrogate A) and (b) a mixture of 73% *n*-dodecane and 27% α -methyl-naphthalene (Surrogate B). The surrogates have been obtained by a constrained optimization approach [7] so as to match their sooting index with that of diesel fuel, since we are interested in the sooting characteristics of diesel fuel

combustion. Table 1 shows a comparison of the properties of the surrogates and that of the target diesel fuel.

TABLE 1: Properties of diesel fuel and surrogates.

Property Name	Diesel Fuel	Surrogate A	Surrogate B
Threshold Sooting Index	29	28.15	29
Cetane Number	45–50 [8]	54	69
H/C	1.93 [8]	1.75	1.85
Liquid density (kg/l)	0.840 [8]	0.791	0.795

The simulations are performed in a constant pressure, spatially homogeneous environment, effectively decoupling the ignition process from the rest of the combustion chamber. The initial temperature is 767 K, $\phi = 3.0$ and the combustion chamber pressure is assumed to be 10 MPa, following the same conditions as that of Westbrook *et al.* [3].

Reaction Kinetics

A single reaction mechanism is obtained for both the surrogates using a component library framework [7]. The kinetic scheme consists of around 250 species and about 1400 reactions. The kinetics of methanol and dimethyl ether are derived from the San Diego mechanism [9]. The mechanisms for the surrogates and the oxygenates are combined using an interactive tool [10]. The combined mechanism is tested for the kinetic description of *n*-dodecane, *m*-xylene, α -methyl-naphthalene (which constitutes the surrogates), as well as methanol and DME and verified to result in similar performance as the reference mechanisms [9, 11].

COMPUTATIONAL RESULTS DISCUSSION

Relevance Of Threshold Sooting Index As A Target For Surrogate Definition

To investigate the importance of TSI as a target in surrogate definition, the rich premixed ignition of surrogate/air mixtures are simulated at $\phi = 3$, $T = 767\text{K}$, and $P = 10\text{MPa}$ using both surrogates in the absence of any oxygenates. Concentrations of the important soot precursor species are plotted for both the surrogates in Fig. 1. As can be observed, the concentration of all the soot precursor species are similar between the two surrogates. This in turn suggests that the surrogates and the real fuel, having nearly the same value of TSI, are likely to have similar amounts of soot precursors in the reactive pool from the rich premixed ignition. In the remainder of the study, surrogate A (Table 1), comprised of *n*-dodecane and *m*-xylene is used to represent the diesel fuel.

Effect Of Addition Of Oxygenates

The above calculations are repeated for cases in which the surrogate fuel is replaced gradually with increasing amounts

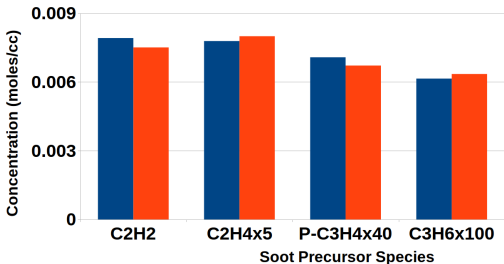


FIGURE 1: Concentrations of soot precursor species obtained with surrogate A (blue bar) and surrogate B (red bar), calculated at an initial temperature of 767K, $\phi = 3$ and $P = 10$ MPa.

of methanol and DME separately. As shown in Fig. 2, just as the surrogate is increasingly replaced by oxygenate, the soot precursor level continues to decrease and becomes insignificant when the oxygen content has reached about 30% of the total mass of the fuel mixture, containing *n*-dodecane and *m*-xylene and the oxygenate (methanol or DME). This *no soot* condition corresponds to a fuel mixture containing 14% surrogate A + 86% methanol and 12% surrogate A + 88% DME, respectively.

It is interesting to note that the oxygen content in the fuel mixture needed to achieve negligible soot precursor in this work is similar to the finding reported by the previous study of Westbrook *et al.* [3] (30% by mass), who neglected the aromatic fraction in diesels, by using *n*-heptane as a surrogate. Further analysis is warranted to make conclusive remarks here, since the reaction mechanisms used in these two studies are significantly different in terms of their soot precursor chemistry descriptions.

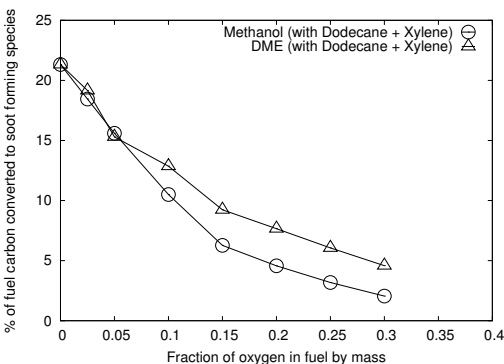


FIGURE 2: Effect of addition of oxygenated species on soot forming species (acetylene, ethene, propene, allene, propyne, cyclopentadiene, propargyl, allyl, cyclopentadienyl, benzene, naphthalene, pyrene)

Reaction Flux Analysis

To understand the change in reaction dynamics concerning soot precursor formation and consumption due to the addition of oxygenates, a path flux analysis is performed here for the case of methanol addition. Since acetylene is the major soot precursor, a flux analysis is performed for this species with two different fuel compositions (a) surrogate A, *i.e.* containing *n*-dodecane + *m*-xylene (baseline case) and (b) 14% surrogate A + 86% methanol by moles (no soot case). The contribution of different pathways to the production and consumption of acetylene is summarized in Fig. 3 for the two cases. Figure 3 clearly depicts that at the no soot condition, more than 85% of acetylene is consumed by reactions with O and OH whereas for the baseline case, most of the acetylene forms vinyl radical (C_2H_3), cyclopentadiene (C_5H_6), and phenyl acetylene ($A_1C_2H_2$), which in turn leads to formation of additional soot precursors and polycyclic aromatic hydrocarbons. Figure 4 further shows that with the addition of oxygenates to the fuel and the corresponding leaner fuel/air mixture ratios, there is a raise in peak temperatures as well as the amounts of radicals (O, OH, H etc.). This increased amounts of radicals now contribute to consuming soot precursor species, such as acetylene, as indicated in the flux analysis presented in Fig. 3.

CONCLUSION

Present study indicates that when significant fractions of diesel fuel are replaced by oxygenated hydrocarbons, the soot precursor levels are reduced to insignificant amounts. But since the fractions of oxygenates required to completely eliminate soot precursor formation are so large, approaching 75–80%, it is practically impossible to attempt this degree of fuel modification in actual diesel engine, nevertheless, this gives valuable insights into the processes leading to soot mitigation.

Our study with the surrogate defined to match the sooting index of the real fuel shows similar results as compared to the work of Westbrook *et al.* [3], who neglected the aromatic fraction in diesels. However further analysis is needed to make conclusive remarks, since the reaction mechanisms used in these two studies are significantly different in terms of their description of soot precursor kinetics.

ACKNOWLEDGMENTS

The last author gratefully acknowledges support from the New Faculty Initiation Grant, Project no. MEE/15–16/845/NFIG offered by the Indian Institute of Technology Madras.

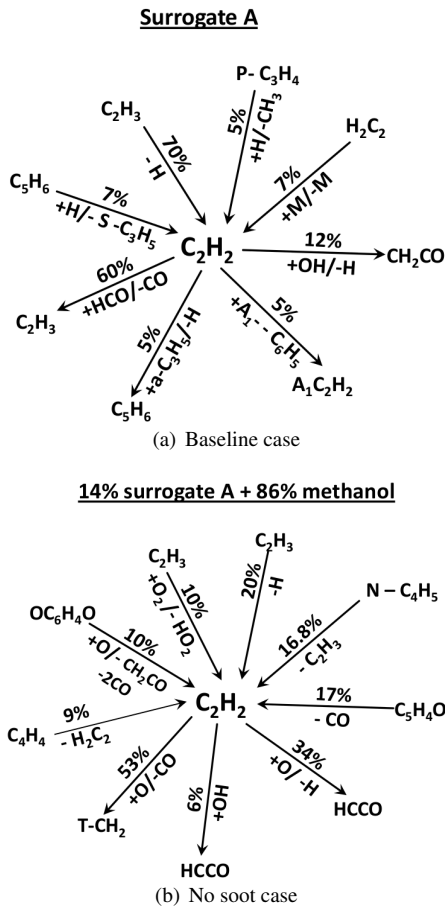


FIGURE 3: Reaction flux analysis for acetylene showing the most significant pathways of production and consumption.

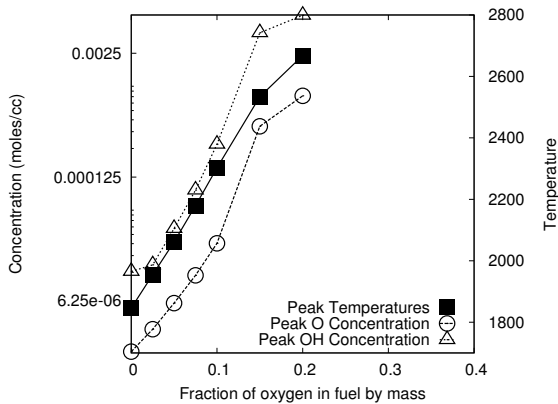


FIGURE 4: Effect of addition of oxygenated species on maximum temperature, peak values of radicals (O, OH).

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