Study of auto-ignition and extinction characteristics of diesel blended with oxygenates in laminar opposed non-premixed flames

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Abstract: Addition of oxygenates to diesel fuel has been found to reduce soot emissions, nonetheless, the resulting changes in the extinction and auto-ignition characteristics of the fuel mixture have not yet been fully understood. The present work investigates this aspect using laminar non-premixed flames. Dimethyl ether and methanol are two oxygenates considered in this study owing to their importance as potential alternative fuels/additives to gasoline and diesel. The fuel stream diluted with nitrogen is injected into a mixing layer from one duct of the counterflow burner, while air is injected from the other duct placed coaxially. The strain rate at extinction is calculated as a function of the mass fraction of fuel in the fuel stream. Further, the temperature of air at auto-ignition is determined as a function of strain rate for a fixed value of the mass fraction of fuel in the fuel stream. These data are obtained for the neat diesel, as well as for the blends of diesel and oxygenates. A flux analysis is used to explain the differences in extinction characteristics upon addition of oxygenates to diesel. A surrogate mixture of *n*-dodecane and *m*-xylene is used to represent the diesel fuel.
Keywords: Diesel, Oxygenates, Extinction, Autoignition

1. Introduction

Emissions from burning diesel continue to be a serious environmental concern. Several strategies have been suggested to tackle, especially the problem of soot emission, one of which, is to alter the fuel composition by the addition of oxygenates [1]. Westbrook *et al.* [2] performed a kinetic study on the reduction of soot emission upon blending diesel with oxygenates. While this is favorable, the effect of the addition of oxygenates on flame stability is not yet understood. In this study, a fundamental analysis is presented to characterize the extinction behaviour of diesel blended with oxygenates, by considering canonical 1D laminar opposed non-premixed flames. Methanol and dimethyl ether (DME) are the oxygenates used in this study.

Methanol is a promising alternative fuel due to its advantages of low price and high oxygen fraction. 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 gas at normal ambient conditions that can be produced from a variety of feed stock. It is non-toxic and environmentally benign. Its high cetane number (>55) makes it particularly attractive as an efficient alternative fuel for use in CI engines. The faster evaporation of DME leads to easier mixing with

air within the engine cylinder and its high oxygen content results in smokeless combustion through low formation and high oxidation rates of particulates [3].

The objective of this study is to investigate the critical conditions of extinction and auto-ignition for neat diesel as well as for blends of diesel and oxygenates using detailed chemical kinetic modeling. A flux analysis is invoked to explain the changes in extinction characteristics upon the addition of oxygenates.

2. Chemical Kinetics Scheme

Diesel is represented by a surrogate consisting of a mixture of *n*-dodecane and *m*-xylene to represent the paraffinic and aromatic hydrocarbon classes in diesel fuels. A component library approach [4] is used to obtain a reaction mechanism for the two surrogate components valid only at high temperatures, consisting of 160 species and 1912 reactions. The kinetics of these components have been validated extensively in homogeneous reactors and premixed flames in Refs. [5, 6]. For the oxygenates, methanol and DME, the San Diego mechanism [7] is used, which consists of 55 species and 249 reactions. A combined kinetics scheme, valid for the diesel and the oxygenates, is obtained by using an automatic tool [8] to combine mechanisms and the resulting model has 176 species and 2157 reactions (counting forward and backward reactions separately).

3. Component Validation

To test the validity of the reaction mechanism, the extinction strain rates and auto-ignition temperatures computed for the individual components, are compared against experimental data available in literature [9, 10] corresponding to a 1D counterflow laminar non-premixed flame. The fuel stream diluted with nitrogen is injected into a mixing layer from one duct of the counterflow burner, while air is injected from the other duct placed coaxially at a small distance. In the experiments and the numerical calculations, the momenta of the counterflowing reactant streams at the boundaries are kept equal to each other. This condition ensures that the stagnation plane formed by the two streams is approximately at the mid-plane between the two ducts. In the region between the stagnation plane and the oxidizer duct, the characteristic strain rate, a_2, defined as the normal gradient of the normal component of the flow velocity, is given by [11],

$$a_2 = \frac{2|V_2|}{L} \left(1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}}\right) \tag{1}$$

where subscripts 1 and 2 denote the fuel and the oxidizer sides, respectively. Computations are performed using FlameMaster [12] with steady plug flow boundary conditions. Figure 1 shows that the extinction strain rate predictions obtained using the assembled mechanism for the individual components, agree well with the available experimental data. A good agreement is also observed for auto-ignition temperatures of methanol compared to experiments, which lie within the experimental uncertainties in the case of *n*-dodecane.

4. Surrogate for Diesel

Owing to the chemical complexity of diesel, a surrogate consisting of a mixture of **65.7% n-dodecane + 34.3% m-xylene** (by mole) is used to kinetically represent diesel. The surrogate has been obtained by a constrained optimization approach [4] so as to match the H/C ratio with
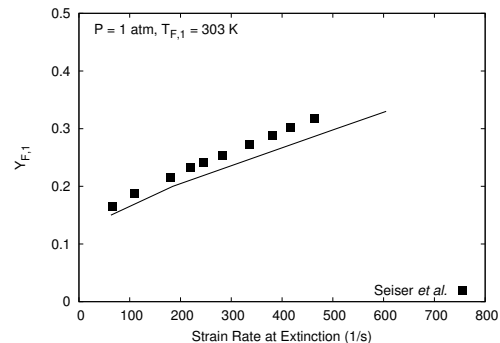
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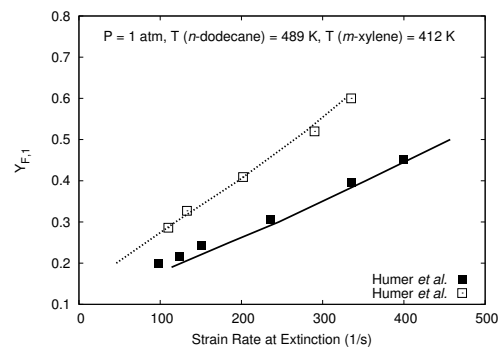
(a) Variation of fuel mass fraction, $Y_{F,1}$, as a function of strain rate at extinction, $a_{2,E}$ for n-dodecane and m-xylene. Experimental data (symbols) from Humer et al. [10], lines present simulation results: n-dodecane (solid), m-xylene (dotted).
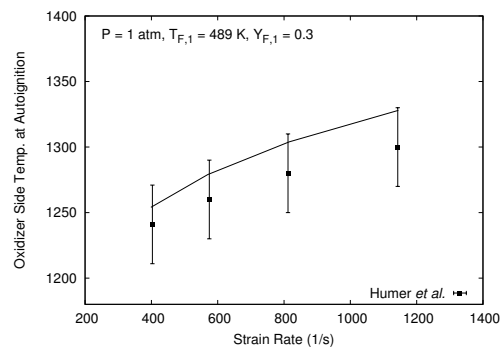
(b) Variation of auto-ignition temperature of air, $T_{2,I}$, as a function of strain rate for n-dodecane. Experimental data (symbols) from Humer et al. [10], lines present simulation results.

(c) Variation of fuel mass fraction, $Y_{F,1}$, as a function of strain rate at extinction, $a_{2,E}$, for methanol; Experimental data (symbols) from Seiser et al. [9], lines present simulation results.
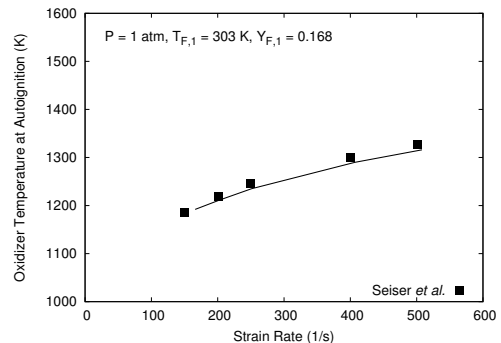
(d) Variation of auto-ignition temperature of air, $T_{2,I}$, as a function of strain rate. Experimental data (symbols) from Seiser et al. [9], lines present simulation results.

Figure 1: Critical conditions of extinction and auto-ignition for individual components: n-dodecane, m-xylene, and methanol.

that of fossil diesel. It may be noted that the molecular weight of surrogate ($148.36\ kg/kmol$) is less than that of diesel (approximately $180\ kg/kmol$), and this is known to impact the extinction behaviour [13]; nonetheless, this surrogate is still appropriate for use in the present study to understand the relative effect of oxygenate addition to diesel towards extinction characteristics qualitatively.

5. Results for diesel and diesel/oxygenate blends

Numerical calculations are performed to obtain the critical conditions of extinction and auto-ignition for diesel and its blends with oxygenates. Firstly, computations are performed for the diesel surrogate and thereafter by considering predefined amounts of oxygenates (methanol and DME) mixed with the surrogate. To understand the variation in the extinction and auto-ignition characteristics with different amounts of oxygenate, simulations are performed with two different

blends of diesel and methanol (5% and 10%). For the extinction cases, the distance between the fuel and oxidizer duct is set as 10 mm, whereas it is set to 12 mm for the auto-ignition cases.

From Fig. 2 it is observed that the strain rate at extinction significantly increases (almost doubles) with the addition of oxygenates, but negligible differences are seen in the auto-ignition temperatures. This is due to the higher reactivity of the blend with oxygenates, which causes a delay in the extinction characteristics as the oxygenates are added. On the other hand, from the auto-ignition data, it is clear that auto-ignition temperature of the diesel surrogate and that of oxygenates are comparable. This is also clear from Figs. 1(b) and 1(d) where in the strain rate range of 400 to 500, auto-ignition temperature of *n*-dodecane and methanol varies in almost the same order, between 1275–1350 K. Also, the extents of variation in these parameters are similar irrsepective of the nature of the oxygenate (methanol or DME) used for blending. Further, Fig. 3 shows that with varying amounts of methanol blended with diesel, the extinction strain rates and ignition temperatures vary only by very small amounts.
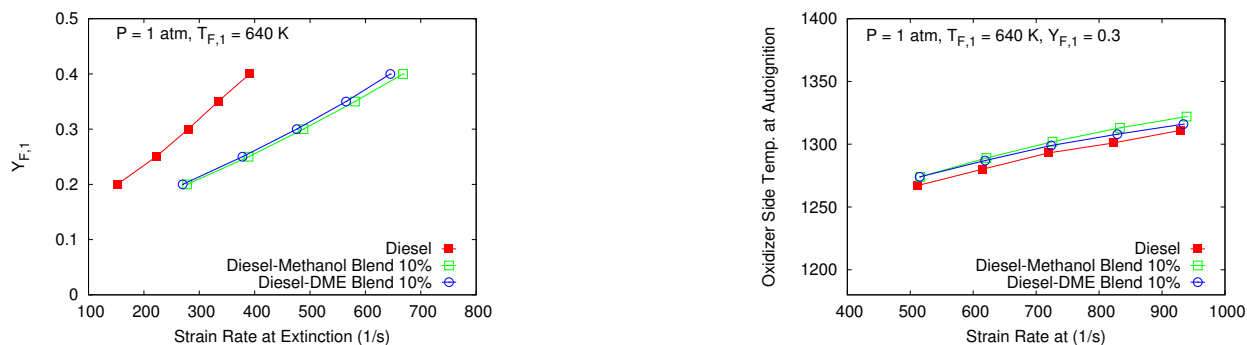

Figure 2: Diesel and blends of diesel and oxygenates: (left) Variation of fuel mass fraction, $Y_{F,1}$, as a function of strain rate at extinction, $a_{2,E}$; (right) variation of temperature of air at auto-ignition, $T_{2,I}$, as a function of strain rate.

5.1 Flux Analysis

To understand the change in reaction dynamics with the addition of oxygenates, firstly, the amounts of H atom, which is the most important radical species and whose transport and subsequent reac-
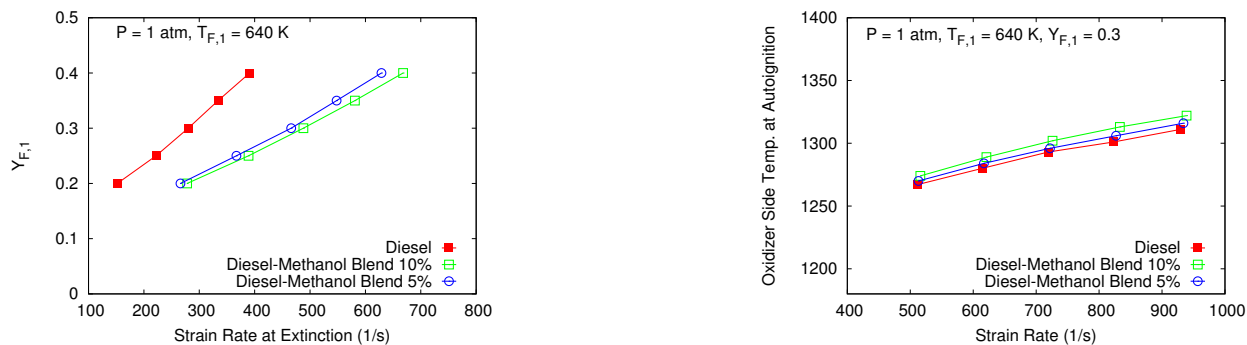

Figure 3: Diesel and its blends with methanol: (left) Variation of fuel mass fraction, $Y_{F,1}$, as a function of strain rate at extinction, $a_{2,E}$; (right) variation of temperature of air at auto-ignition, $T_{2,I}$, as a function of strain rate.

tions with the fuel govern the flame, are compared between the cases of diesel vs. diesel-methanol blends as shown in Fig. 5(a). Indeed, from Fig. 5(a), it is observed that the amount of H atoms are higher in the case where some oxygenate is present, which directly translates into a more vigorous reaction for the same strain rate, and consequently a larger value for extinction strain rate.
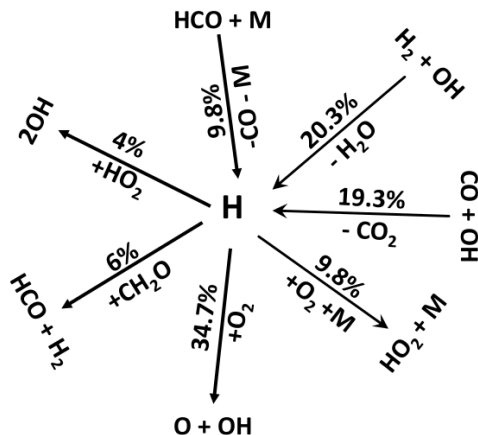

Figure 4: Pathways for H atom consumption and production for diesel-methanol blend (10 %) obtained at P = 1 atm, $Y_{F,1}$ = 0.2, and a_2 = 262 $1/s$.
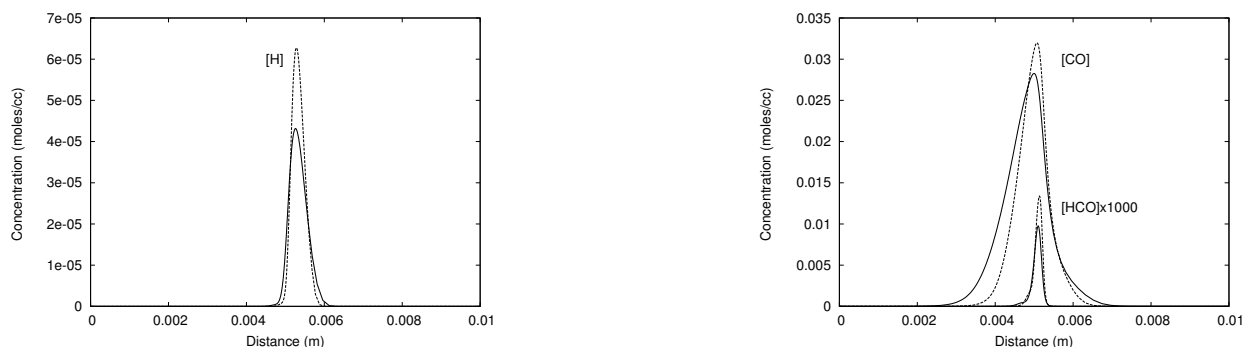

Figure 5: (left) Change in [H] with distance; (right) change in [CO] and [HCO] with distance. Solid lines represent neat diesel fuel and dashed lines represent diesel-methanol blend (10%).

A path flux analysis has been performed to elucidate this further. The results presented in Fig. 4 reveals that significant amount of H atom is produced from HCO and CO. It is well-established that the oxidation pathway of methanol yields HCO and CO as,

$$CH_3OH \rightarrow CH_2OH \rightarrow CH_2O \rightarrow HCO \rightarrow CO.$$
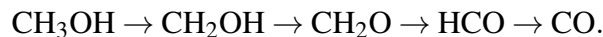
This explains the larger amounts of HCO, CO in the presence of methanol in the fuel blend (see Fig. 5(b)), and therefore, large amounts of H atoms, and hence increased extinction strain rates. A similar trend is observed when diesel is replaced by DME.

6. Conclusions

The above results reveal that blending small amounts of oxygenates with diesel increases its resistance to extinction, which can be of use in applications such as burners, furnaces and pre-vaporizers. Also, the added advantage of blending oxygenate to diesel is that it helps in reducing

soot. However, the auto-ignition characteristics are not altered much due to blending. This study suggests that in the presence of oxygenate, a combustion system can be made more stable even at higher strain rates and at the same time operate with reduced emissions.

7. Acknowledgements

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