Effect of dimethyl ether (DME) addition on sooting limits in counterflow diffusion flames of ethylene at elevated pressures

Zepeng Li^a, Hafiz M. F. Amin^a, Peng Liu^{a*}, Yu Wang^b, Suk Ho Chung^a, William L. Roberts^a

^aKing Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center, Thuwal, Saudi Arabia

^bSchool of Automotive Engineering, Wuhan University of Technology, Wuhan, China

Abstract

The effects of dimethyl ether (DME) addition to ethylene fuel on sooting tendencies with varying pressure were investigated in counterflow diffusion flames by using a laser scattering technique. Sooting limit maps were determined in the fuel (X_F) and oxygen (X_O) mole fraction plane, separating sooting and non-sooting regions. The results showed that when DME is mixed to ethylene, the sooting region was appreciably shrank, especially in the cases of soot formation/oxidation (SFO) flames as compared with the cases of soot formation (SF) flames. This indicated an inhibiting role of DME on sooting. An interesting observation was that the critical X_O required for sooting initially decreased and then increased with the DME mixing ratio to ethylene β for the cases of SF flames, exhibiting a non-monotonic behavior. This implied a promoting role of DME on sooting when small amount of DME is mixed to ethylene. As the pressure increased, the sooting region generally expanded. Specifically, the range of β in promoting soot formation extended with pressure. This implies that a strategy in reducing soot by adding DME to ethylene at high pressures required a large amount of DME addition. To interpret the observed phenomena, kinetic simulations including reaction pathway and sensitivity analyses were conducted with the opposed-flow flames model using the KAUST-Aramco PAH Mech. The results showed that the thermal effect of DME addition on sooting tendency monotonically decreases with β . The chemical effect was found to be the main contributor to the DME addition effect on sooting tendency, resulting in the non-monotonic sooting limit behavior. The pathway analysis showed the role of methyl radicals generated from DME promoted incipient benzene ring formation when small amount of DME was added, which can be attributed to the soot promoting role of DME addition for small β .

Keywords

Soot, Sooting limit, Dimethyl ether (DME), High pressure, Counterflow diffusion flame

1. Introduction

The combustion of fossil fuels provides energy, while accompanying hazardous emissions such as particulate matters and nitric oxides pose threats to the environment [1-4]. In particular, soot emission has been recognized to play detrimental roles on global warming and human health. To develop technologies for soot reduction, physical mechanisms of soot formation and oxidation at conditions relevant to practical combustion devices should be understood, which has motivated extensive studies on dominant factors controlling soot formation [5-9].

Fuel structure is one of the important factors that affect soot formation and thus the sooting propensity [10-16]. In this regard, several quantitative metrics have been proposed, including the threshold soot index (TSI) [10] and the yield soot index (YSI) [17], which are mainly based on coflow flames or the smoke points of pure fuels and air. Recently, a sooting limit map was investigated in counterflow diffusion flames (CDFs) by adopting light extinction/scattering techniques. Critical oxygen and fuel mole fractions [18, 19] required for sooting were determined, from which the sooting temperature index (STI) and sooting sensitivity index (SSI) [19] were proposed. They revealed that the sooting tendency increased with the number of carbon atoms of fuels at a specified strain rate, and alkane fuels showed a lower sooting tendency than alkene fuels with the same number of carbon atoms.

Dimethyl ether (DME) is generally considered as a promising fuel additive or alternative fuel [4, 20-26] because of low particulate emission, low auto ignition temperature, and rapid vaporization upon injection, which comes from its high cetane number (55–60) (suitable for compression ignition engines), high oxygen content (35 wt%), low boiling point (249 K), and relatively low vapor pressure (easy to handle and transport) characteristics. Additionally, DME can be produced from diverse sources such as natural gas, coal gasification, oil residues, and biomass [20]. The possibility of reduction of harmful emissions with DME addition was investigated in various laboratory scale flames and engine studies [27-30]. The flame structure and species composition with DME blending in iso-octane fuel was investigated experimentally and numerically in premixed low-pressure flames, and they revealed that the addition of DME decreased the formation of soot precursors while enhanced the production of formaldehyde [29]. However, in counterflow diffusion flames, a small amount of DME addition to ethylene fuel enhances the formation of small aromatic precursors and soot particles in the pyrolysis region based on laser-induced fluorescence and incandescence techniques [22, 24]. These studies were mainly conducted under atmospheric or low-pressure conditions. Considering that pressure plays a crucial role in overall soot yield and

practical combustion devices generally operated under high pressures [31, 32], it is important to extend the DME mixing effect on sooting tendency to higher pressures.

In the present work, we systematically investigated the effect of DME addition to ethylene fuel in counterflow diffusion flames. Note that ethylene fuel has been extensively investigated for soot studies both experimentally and numerically including soot modeling [5, 12]. Sooting limits were determined using a laser scattering technique and the effect of pressure was studied. Further, numerical simulation was conducted to provide chemical kinetic insights of the experimental observations.

2. Experiment and simulations

The apparatus consisted of counterflow burners, a flow control system and a laser light scattering setup. Two counterflow burner setups were employed, one dedicated at atmospheric pressure and the other for operation at elevated pressures. Atmospheric-pressure experiments were conducted on both burners to test the setup-dependency in sooting limit measurement.

The atmospheric-pressure counterflow burner (Setup 1) had a pair of contoured nozzles with an exit diameter of $d = 10$ mm and a separation distance of $l = 8$ mm. Concentric slits with 2 mm width supplied shield nitrogen to prevent interference from ambient air. The high-pressure burner (Setup 2) was enclosed in a pressure vessel, and had $d = 8.5$ mm and $l = 8$ mm. The width of the concentric slit for shield nitrogen was 9 mm. The pressure vessel had four optical windows providing 160° of optical access, whose details were reported previously [33]. An electronic back-pressure regulator controlled the vessel pressure within 2% fluctuations at a setpoint. Nitrogen flow across the optical windows prevented soot particle accumulation, however, routine cleaning of the windows was required to ensure data quality. For all flames in both setups, the global strain rate (a) was maintained at 50 s^{-1} , which was calculated based on the nozzle exit velocity ($U_0 = 20 \text{ cm/s}$) and $l/2$ [34]. The flow rates of all gases were controlled by thermal-based mass flow controllers. Due to the saturated vapor pressure of DME (about 5 atm at room temperature), the maximum pressure investigated in this work was limited to 3.5 atm for a stable operation. At higher pressures, an appreciable flame fluctuation was observed due to the vapor pressure issue. A future study is required at higher pressure by resolving this issue.

For the laser light scattering setup, an Argon-ion laser (514.5 nm) was used as the light source, and lock-in amplifiers coupled with a mechanical chopper were utilized to improve the signal-to-noise ratio. The optical system was aligned to provide a uniform laser beam with a diameter of 100 μm . To monitor the laser intensity fluctuation, a reference signal was monitored by a photodiode. The scattering signal was measured by a photo-multiplier tube (PMT) at 90° to the incident light. As spurious laser reflections from other material surfaces may induce errors in the scattering signals, signal testing using three gases (nitrogen, propane, and helium) was conducted following ref. [35]. Helium (99.9999 %) was regarded as the background case due to its extra-small (≈ 0) scattering cross-section relative to other gases. Since the actual scattering cross-section of helium was not exactly zero, the method could slightly overestimate the ratio of propane to nitrogen of 13.6, which was acceptable in determining sooting limits (this ratio was 12.7 in [35]).

The fuel stream was composed of ethylene (>99.9 %), DME (>99.9 %), and nitrogen (99.9999 %), while the oxidizer stream was oxygen (99.9995 %) and nitrogen. In the following, X_F (X_O) represent the fuel (oxygen) mole fractions in the fuel (oxidizer) stream with the rest of nitrogen in each stream. The DME mixing ratio (β) in the fuel stream was defined as the ratio of volumetric flow rates between DME and mixture fuel (ethylene+DME).

To investigate the potential reasons for the effect of DME addition on sooting limits especially at elevated pressures, kinetic simulations including reaction pathway analysis and sensitivity analysis were conducted using the opposed-flow module [36] in Chemkin-Pro package. The boundary conditions and other relevant input parameters used in the simulations were determined from the experimental conditions. Specifically, the simulated flame conditions were set to a global strain rate $a = 50 \text{ s}^{-1}$, the inlet temperature was $T_{\text{in}} = 298 \text{ K}$, and the pressure ranged from $P = 1$ to 5 atm. The kinetic mechanism used here was KAUST-Aramco PAH Mech [37], where the base mechanism is AramcoMech 1.3 [38] validated against the DME/O₂/N₂ flame at high pressure (12.5 atm). Since the experiments were conducted at soot onset conditions, only gas-phase reactions were considered in the simulation.

3. Results and discussion

Scattering signal is sensitive to particle size, thus the scattering intensity from soot particles is significantly larger than that from gas molecules. Based on this, sooting limit can be determined by varying X_F and X_O following

the method detailed in [18, 19]. Figure 1 shows a typical procedure in determining sooting limits, where the scattering signal along the centerline of the burner was recorded at a spatial increment of 0.1 mm for the baseline ethylene flame ($\beta = 0$). The critical oxygen mole fraction ($X_{O,cr}$) at sooting limit is determined at a specified X_F by varying the oxygen content at which the scattering signal varies drastically. In some cases, a critical fuel content ($X_{F,cr}$) was determined at a specified X_O .

The scattering signals at the atmospheric pressure for $X_F = 1.0$ at several X_O are shown in Fig. 1a, along with direct images of corresponding flames in the insets. At $X_O = 0.16$, the scattering signal monotonically decreases from the fuel to the oxidizer side, as a result of the larger gas-phase scattering cross-section of the fuel molecule C_2H_4 than that of the oxidizer. At $X_O = 0.17$, a local maximum appears due to the particle scattering from soot, which is also confirmed by the orange-color luminescence emitted by heated soot particles. This first appearance of the local maximum is judged as the critical sooting condition. A higher concentration of O_2 contributes to the increase in flame temperature and production of radical species in counterflow flames, which promotes incipient ring formation for soot inception and subsequent growth along with H abstraction from soot surface generating more active site for soot growth [39, 40]. This may explain why the oxygen concentration has to exceed a threshold for soot formation to occur. As will be explained in detail later, these flame conditions correspond to the soot formation (SF) flame [41], where the flame is located on the oxidizer side from the stagnation plane, thus the convection is toward the fuel side in the region between the stagnation plane and flame. Since the concentrations of oxidizing species such as OH and O_2 are very low, oxidation effects on soot are minimal. A further increase in $X_O = 0.18$ results in a significant increase in the magnitude of the local maximum due to appreciable soot formation. At 3.5 atm (Fig. 1b) with $X_F = 0.75$, an increment of 0.01 of X_O leads to a larger change in the scattering signal. Both the sensitivity of scattering signal to X_O and the variation of flame color are more obvious at higher pressures. Since the increment of X_F and X_O is 0.01 (or 1%), the uncertainty in the sooting limit for $X_{F,cr}$ or $X_{O,cr}$ is ± 0.005 .

Fig. 1. Illustration in determining critical oxygen mole fraction ($X_{O,cr}$) at specified X_F (global strain rate = 50 s^{-1}).

As the present work attempts to measure sooting limits in counterflow flames at elevated pressures, it is essential to confirm an apparatus dependence. In this regard, the sooting limit maps as obtained with both burners are compared with that obtained by Wang and Chung [19], and the results are shown in Fig. 2 for the baseline ethylene flames. The sooting limit curves divide the whole X_F – X_O plane into two regions: upper right being sooting region and the rest non-sooting. The agreements among the maps indicate the good repeatability of the sooting limit measurements, and that the experimental apparatus has minimal effect on the sooting limits. Additionally, flame temperatures were calculated from Chemkin- Pro [36] for 153 counterflow flames by varying X_F and X_O , and iso-flame temperature lines were drawn in the lines along with the color-coding. Note that the previously measured temperature profiles using a coherent anti-Stokes Raman spectroscopy (CARS) agreed satisfactorily with calculated ones [41]. Also, a good agreement was reported between the calculated flame temperatures and experimental ones using acoustic emissions from laser-induced plasmas [42].

Fig. 2. Comparison of sooting limit maps of ethylene flames using different experimental setups and simulated flame temperature contours.

Sooting structures of counterflow diffusion flames can be drastically different depending on the relative position of a flame to the stagnation plane such that two distinct flame types can be defined [41]: soot formation (SF) flame and soot formation/oxidation (SFO) flame. The boundary of SF and SFO flame is calculated based on the stoichiometric mixture fraction [43], and marked as the dotted line in Fig. 2. In a SF flame (large X_F and small X_O), the flame is located on the oxidizer side of the stagnation plane (refer to the schematic in the inset). Since soot is formed on the fuel side of the flame, newly incepted soot particles shall be transported toward the fuel side without much oxidation, and finally, they will leak through the stagnation plane. Since soot formation is very sensitive to flame temperature [39], the sooting limit curves in Fig. 2 closely follow iso-flame temperature contours for SF flames with large X_F [23]. While a SFO flame is located on the fuel side of the stagnation plane, and the soot particles formed will be convected through the flame toward the stagnation plane and oxidized by such species as O_2 , OH , and O . In the SFO region, the flame temperature increases significantly along the sooting limit curves as X_O increases, which results from the competition between temperature sensitive soot formation rate and soot oxidation rate [9].

3.1 Effect of DME addition

The effect of DME addition to ethylene on sooting limit is examined. Figure 3a shows the sooting limit maps with varying the DME mixing ratio β for the atmospheric-pressure flames. The three curves of sooting limit at $\beta=0$, 0.02, and 0.05 are nearly overlapped. As β further increases (0.1 to 0.5), it is evident that the sooting region shrinks with increasing β , indicating that the addition of DME into ethylene can reduce the sooting tendency.

Since the strain rate is kept constant for all flames, dilution, thermal and chemical effects are expected to contribute to the observed differences of sooting limit curves. From the flame temperature contours in Fig. 2, in the SF region, the flame temperature changes little along the sooting limit curve, such that the thermal effect in this region is expected to be small, hence the variation of $X_{O,cr}$ on sooting limit is expected to be small. In the SFO region, the flame temperature increases significantly along the sooting limit curve as X_O increases. The competition between soot oxidation and soot formation can be attributed to the temperature rise, thus both thermal and chemical effects are expected to contribute to the sooting limit (X_F), resulting in the larger variation of X_F in the SFO flames.

With the addition of DME, the variation of sooting limit ($X_{O,cr}$) is much smaller in SF flames at a specified X_F , than that of $X_{F,cr}$ in SFO flames for large X_O . Another interesting feature is that as β increases, the bending behavior of the sooting limit curve toward larger X_F becomes more pronounced. One potential reason for the bending tendency in high X_O region is that the soot oxidation is enhanced at higher flame temperature in SFO flames. As a result, more fuel is needed to balance the soot formation and oxidation processes. When β increases, the flame temperature increases as well, so the bending is more pronounced due to higher oxidation rate.

Fig. 3. Sooting limit map at several β (a) and critical oxygen mole fraction ($X_{O,cr}$) with DME mixing ratio at several X_F (b) in the atmospheric-pressure burner.

The dilution effect of nitrogen on sooting propensity can be examined. The critical oxygen mole fraction $X_{O,cr}$ is plotted with the DME mixing ratio in Fig. 3b at several X_F values. As X_F decreases having more dilution with nitrogen, the required $X_{O,cr}$ increases. This can be explained based on the decreasing effect of N_2 dilution in the fuel stream on flame temperature, which is compensated by the increasing effect of higher O_2 requirement in the oxidizer stream. It is interesting to note that for a specified X_F , $X_{O,cr}$ first decreases (although the variation is small) and then increases with β . Here, the points are experimental data, and the lines are the corresponding quadratic fitting, and the inset shows the coefficients of the quadratic term.

Generally speaking, higher $X_{O,cr}$ with β for a specified X_F indicates more oxygen is needed to produce soot; in other words, the sooting propensity decreases. As DME is added to the ethylene flames, $X_{O,cr}$ decreases with β (the

sooting propensity increases), reaches a minimum around $\beta = 0.05$, and then increases for $\beta > 0.05$. This sooting limit behavior is consistent with the previous soot volume fraction measurement for specified X_F and X_O inside the sooting region [24], where the soot volume fraction initially increases and then decreases with β , resulting in the synergistic effect. This means that a certain mixture of ethylene and DME generates more soot than the respective fuels. This point will be further elaborated later.

The data shows with the increment of $\Delta X_F = 0.15$. The result clearly shows that the influence on $X_{O,cr}$ becomes more pronounced as X_F decreases with the fixed ΔX_F . This implies that when the fuel (or carbon flow) is diluted by nitrogen, the dependence of dilution on sooting tendencies increases. For the inset in Fig. 3b, there is a negative relationship between the quadratic term coefficient with the fuel mole fraction in the quadratic curve fittings. That means as X_F decreases, the increase of $X_{O,cr}$ with respect to DME mixing ratio becomes more sensitive, meaning that the dependence of DME addition on sooting tendency increases as the fuel is diluted.

3.2 Effect of pressure

Pressure plays an important role in sooting tendency, hence the effects of pressure and DME addition and their interactions on sooting limits are examined. The variation of sooting limits with pressure and β is shown in Fig. 4. The result shows that the sooting regions are notably extended as the pressure increases, indicating an increase in the sooting propensity. Moreover, the variation of $X_{O,cr}$ with pressure is much smaller when $X_F = 1$ than that of $X_{F,cr}$ when $X_O = 1$. At $X_F = 1$, the increases in $X_{O,cr}$ when the pressure increases from 1 to 3.5 atm are 0.045, 0.045, 0.035, and 0.040 for $\beta = 0, 0.1, 0.3$, and 0.5 , respectively. At $X_O = 1$, the increases in $X_{F,cr}$ with the same pressure change are 0.075, 0.08, 0.085, and 0.1 for $\beta = 0, 0.1, 0.3$, and 0.5 , respectively. This implies that the dependence of pressure is rather modest in the SF flames, irrespective of the DME mixing ratio. While in the SFO flames, DME addition is sensitive to pressure on the sooting limits.

Fig. 4. Sooting limit maps with respect to DME mixing ratios (β) at $P=1, 2$ and 3.5 atm. Experiments operated in the pressurized-counterflow burner.

As shown in Fig. 3b, there is a critical DME mixing ratio (β_{cr}) at which $X_{O,cr}$ has its minimum for $X_F = 1$. When $\beta > (<) \beta_{cr}$, the addition of DME decreases (increases) the sooting propensity. To further substantiate the critical DME mixing behavior and to examine the effect of pressure on β_{cr} for the pressurized counterflow flames, the normalized maximum scattering intensity with β at various pressures is investigated and shown in Fig. 5. Using Fig. 1a as an example to demonstrate the method to obtain Fig. 5: the scattering intensity for $X_O = 0.16$, which only contains the scattering signal of gases, is subtracted from the curve for $X_O = 0.17$ to determine the net scattering intensity at $\beta = 0$. For each β , several net scattering intensities are acquired from repeated measurements at the flame conditions close to the corresponding sooting limits. Then, the recorded peak net scattering intensities at the same pressure are normalized by the maximum value among all the intensities of different β s. Quadratic fittings of the experimental data are also marked. At $P=1, 2$, and 3.5 atm, the maximum scattering intensity in pressurized counterflow burner appears at $\beta_{cr}=0.057, 0.106$, and 0.144 with the correlation coefficients of $R^2 = 0.787, 0.806$, and 0.739 , respectively, indicating that β_{cr} increases with pressure. This means that the range of β in increasing soot propensity with DME addition expands with pressure, implying that an effort to reduce soot by adding DME to ethylene may not be effective at very high pressures, i.e., a larger amount of DME addition is required to achieve soot reduction for the

ethylene flames. Considering that the pressures in practical devices such as I.C. engines and gas turbines are much higher than those in the present experiments, a further experiment should be conducted under higher pressures.

Fig. 5. Sooting propensity with DME mixing ratio at several pressures. Dashed lines indicate quadratic fittings with the 95% confidence bands.

3.3 Kinetic analysis

To better understand the effect of DME addition on sooting limits, a detailed analysis of the underlying physics is discussed here. The dilution, thermal and chemical effects are expected to be accounted for the observed sooting propensity with DME addition [44]. The effect of dilution mainly reflects on the chemical and thermal aspects in this study, since the collider effect (i.e., $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3 + \text{CH}_3\text{O} (+\text{M})$ (R330 in the KAUST-Aramco PAH Mech), the reaction rate is faster with the existence of a third-body as the collider) of DME is very weak in polycyclic aromatic carbon (PAH) and soot formation region due to the low concentration. Therefore, the chemical and thermal effects of DME addition to soot formation are focused here.

To quantify the effect of DME addition on sooting limits, thermal and chemical effects are isolated in the simulations. A fictitious DME (FDME) is introduced in the simulation, which has the same thermodynamic and transport properties with DME but is not participating in any chemical reactions. Benzene (C_6H_6), regarded as one of the most important precursors of soot, is selected to represent soot formation characteristics [45]. In this strategy, the chemical effect of DME addition on the soot formation can be identified by comparing benzene mole fractions from the simulations with FDME and DME. The thermal contribution can be evaluated through subtracting

chemical effect from the total effects. In the simulation, X_F and X_O are set to 0.7 and 0.19, respectively. The thermal and chemical contributions to benzene production at several flame conditions are presented in Fig. 6 for $P = 1$ and 3 atm. Note that the thermal contribution of DME addition (treating DME as diluent) monotonically decreases with β as expected. While the chemical contribution increases first, then decreases after reaching a peak value. The trend of the chemical factor is the same with the trend of the overall effect of DME addition, which implies that the synergistic effect of DME addition on soot formation is dominantly controlled by its chemical effect instead of the thermal effect. This is also evidenced by the relatively large difference between the benzene mole fractions coming from the chemical and thermal effects. For example, the mole fraction of benzene generated from the isolated chemical effect is higher than that from the thermal effect by a factor of 3.5 when $\beta = 0.5$ at $P = 1$ atm, and this ratio increases to 5.6 at $P = 3$ atm. It is observed that the benzene formation is greatly enhanced at higher pressure, and the chemical contributions to benzene formation become more pronounced at higher pressure. This analysis supports the observed pressure-dependence of soot formation with DME addition discussed previously.

Fig. 6. Maximum mole fraction of benzene against mixing ratio indicating thermal and chemical contributions to benzene production at $P = 1$ and 3 atm, (X_F and X_O are set to 0.7 and 0.19, respectively, in simulation).

For further insights on how the chemical effect of DME addition contributes to soot formation, the sensitivity analysis of DME entrance reactions towards benzene formation is conducted by separately decreasing their reaction rate coefficients by a factor of 10. The result is shown in Fig. 7a. The reactions $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3 + \text{CH}_3\text{O}$

(+M) (R330), $\text{CH}_3\text{OCH}_3 + \text{H} = \text{CH}_3\text{OCH}_2 + \text{H}_2$ (R332), and $\text{CH}_3\text{OCH}_3 + \text{CH}_3 = \text{CH}_3\text{OCH}_2 + \text{CH}_4$ (R335) are the dominant reactions influencing benzene formation with DME addition among nine DME entrance reactions in KAUST-Aramco PAH Mech. Specifically, benzene formation is appreciably enhanced by the CH_3 production reaction (R330) and H radical consumption reaction (R332) when $\beta = 0.2$ and 0.5 , and is suppressed by the CH_3 consumption reaction (R335). The sensitivity results indicate that the benzene formation is sensitive to the productions of CH_3 and H radicals.

To explore the role of CH_3 and H, the reaction pathway analysis is carried out for benzene formation. The result shows that the formation of benzene is dominantly controlled by addition reactions of $\text{C}_4\text{H}_x + \text{C}_2\text{H}_2$ and partially controlled by the propargyl recombination reaction $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ in the benzene formation region. As shown in Fig. 7b, when $\beta = 0$, 76.8% benzene is produced from the reaction of $\text{C}_4\text{H}_5 + \text{C}_2\text{H}_2$ and $\text{C}_4\text{H}_6 + \text{C}_2\text{H}_3$, only 7.3% from the reaction of $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ at the location of maximum benzene mole fraction; when $\beta = 0.5$, the contribution of $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ reaction in benzene formation increases to 19.3%. The enhanced contribution of $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ reaction in benzene formation results from the higher production of CH_3 radical with DME addition, as the sensitivity analysis showed that C_3H_3 is mainly formed from the pathway of $\text{CH}_3 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_4 \rightarrow \text{C}_3\text{H}_3$ in our flame case. Also note that C_2H_2 and C_2H_3 are the main precursors for the formation of C_4H_5 and C_4H_6 in these flames. Here, the C_2H_2 radical is mainly produced from the base C_2H_4 fuel by the reactions of $\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$ and subsequently $\text{C}_2\text{H}_3 (\text{M}) = \text{C}_2\text{H}_2 + \text{H}$. Higher CH_3 concentration is more favorable for the reaction of $\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$ to produce C_2H_3 , and a lower H concentration is likely to increase the yield of C_2H_2 from the reaction of $\text{C}_2\text{H}_3 (\text{M}) = \text{C}_2\text{H}_2 + \text{H}$ in view of reaction balance. Therefore, the chemical effect of DME addition on soot formation is realized by the pathway of $\text{DME} \rightarrow \text{CH}_3(\text{H}) \rightarrow \text{C}_2\text{H}_2(\text{C}_3\text{H}_3) \rightarrow \text{C}_6\text{H}_6 \rightarrow \text{soot}$ with the assistance of the entrance reactions of $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3 + \text{CH}_3\text{O} (+\text{M})$ (R330), $\text{CH}_3\text{OCH}_3 + \text{H} = \text{CH}_3\text{OCH}_2 + \text{H}_2$ (R332), and $\text{CH}_3\text{OCH}_3 + \text{CH}_3 = \text{CH}_3\text{OCH}_2 + \text{CH}_4$ (R335).

The present analysis is mainly for soot formation flames, where the DME decomposition and benzene formation occur on the fuel side of flame, the DME oxidation effect is minimal since OH, O and O_2 concentrations are very low. The oxygen in DME is going through $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$ (note that complete pyrolysis products of DME at equilibrium are CH_4 , CO and H_2). Thus, the oxygen in DME does

not involve in the benzene formation (mainly through $C_2 \rightarrow C_4 \rightarrow \text{benzene}$ and $CH_3 \rightarrow CH_2 (+C_2 \text{ species}) \rightarrow C_3H_3$ and its recombination to benzene) leading to soot formation.

Note that the present synergistic effect by DME addition to ethylene can be attributed to the formation of CH_3 radicals from DME. DME mixing with other gaseous hydrocarbon fuels (such as CH_4 , C_2H_6 , C_3H_8) and long chain hydrocarbons such as n-heptane have discussed previously [24] Since CH_3 are readily produced, such synergistic effect with DME addition by the interplay of C_2H_2 and C_3H_3 (via CH_3 paths: $CH_3 \rightarrow CH_2 (+C_2 \text{ species}) \rightarrow C_3H_3$) was not observed.

Fig. 7. Sensitivity analysis of DME entrance reactions towards benzene formation (a), and reaction pathway analysis of benzene formation (b) (X_F and X_O are set to 0.7 and 0.19, respectively, in simulation).

The above kinetic analysis indicates that soot formation behavior may be captured by the formation of C_6H_6 and C_2H_2 . To acquire further insights on how the quantitative effect of DME on sooting tendency varies with pressure, the maximum concentrations of C_6H_6 and C_2H_2 at various pressures and DME mixing ratios are plotted in Fig. 8. With the increase in β at a specified pressure, the maximum concentration of benzene first increases, reaching a peak value and then decreases (a). The benzene formation is very sensitive to pressure, the rate of increase in the maximum concentrations of C_6H_6 along β is faster at higher pressure when β is lower than 0.2. Additionally, the peak of the benzene concentration profile is also seen to shift to the higher β as pressure increases, which implies that more DME is needed to suppress benzene formation at higher pressures. As for C_2H_2 (b), higher pressure tends to accelerate acetylene production, and enhance C_6H_6 formation.

Fig. 8. Maximum concentration profiles of C_6H_6 (a) and C_2H_2 (b) with DME mixing ratios at several pressures (X_F and X_O are set to 0.7 and 0.19, respectively, in simulation).

The critical DME mixing ratios (β_{cr}) for maximum concentrations of C_6H_6 and C_2H_2 are determined and shown in Fig. 9. The $\beta_{cr,benz}$ ($\beta_{cr,acet}$) is defined as the critical DME mixing ratio (β) corresponding to the peak of C_6H_6 (C_2H_2) concentration profile in Fig. 8. These critical values of $\beta_{cr,benz}$ and $\beta_{cr,acet}$, and the measured β_{cr} corresponding to the highest sooting tendency in Fig. 9 are plotted as a function of pressure. From 1 atm to 2 atm, the variations of β_{cr} of the calculated benzene, calculated C_2H_2 and experiments are 0.057, 0.026, and 0.052, respectively. The variation of $\beta_{cr,benz}$ with pressure is qualitatively similar to that of β_{cr} from experiments. On the other hand, as the pressure increases, $\beta_{cr,acet}$ increases first, then decreases for $P > 2.5$ atm, revealing a non-monotonic behavior, which is qualitatively different from the experimental β_{cr} behavior. These trends of β_{cr} , $\beta_{cr,benz}$ and $\beta_{cr,acet}$ suggest that the soot formation may be better described by the concentration of benzene instead of C_2H_2 [46-48].

Fig. 9. Critical DME mixing ratios at maximum simulated concentrations of C_6H_6 ($\beta_{cr,benz}$) and C_2H_2 ($\beta_{cr,acet}$), and measured β_{cr} with respect to pressure. To fit all curves with one axis, the $\beta_{cr,acet}$ and β_{cr} are added 0.15.

4. Conclusions

To investigate the synergistic effect of DME addition on sooting tendency at elevated pressures, the critical X_F – X_O based sooting limit maps of ethylene/DME flames for 1–3.5 atm are determined using a laser scattering technique in counterflow diffusion flames. Numerical modeling studies were performed to elucidate the experimental observations. The major conclusions of the present study are as follows:

1. Sooting tendency is more sensitive in SFO flames than in SF flames due to the competition between soot formation and oxidation. The dependence of pressure is relatively mild in SF flames irrespective of DME addition. While in SFO flames, the pressure-dependence of sooting limits with DME addition is stronger.
2. When the fuel (or carbon flow) is diluted, the dependence of dilution on sooting tendencies increases. That is, as X_F decreases, the increase of $X_{O,cr}$ with respect to DME mixing ratio becomes more sensitive, meaning that the effect of DME addition on sooting tendency is more obvious as the fuel is diluted.
3. The sooting limits (X_F and X_O) are sensitive to pressure, and the sooting tendency increases at higher pressure. The range of β in increasing soot propensity with DME addition expands with pressure, thus the effort to reduce soot by doping DME to ethylene may not be effective at high pressures.
4. Kinetic analysis indicates that sooting limit with DME addition is dominantly determined by the synergistic chemical effect, which is likely realized by the pathway of $DME \rightarrow CH_3(H) \rightarrow C_2H_2(C_3H_3) \rightarrow C_6H_6 \rightarrow soot$ with the assistance of the entrance reactions of $CH_3OCH_3 (+M) = CH_3 + CH_3O (+M)$ (R330), $CH_3OCH_3 + H = CH_3OCH_2 + H_2$ (R332), and $CH_3OCH_3 + CH_3 = CH_3OCH_2 + CH_4$ (R335).

Acknowledgment

This research was supported by King Abdullah University of Science and Technology (KAUST). The work at the Wuhan University of Technology was supported by the National Key R&D Program of China (2017YFC0211201) and the National Natural Science Foundation of China (51606136).

References

- [1] I.M. Kennedy, The health effects of combustion-generated aerosols, *Proc. Combust. Inst.* 31 (2007) 2757-2770.
- [2] J.S. Gaffney, N.A. Marley, The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond, *Atmos. Environ.* 43 (2009) 23-36.
- [3] Y. Liu, J. Liggio, S.M. Li, D. Breznan, R. Vincent, E.M. Thomson, P. Kumarathasan, D. Das, J. Abbatt, M. Antinolo, L. Russell, Chemical and toxicological evolution of carbon nanotubes during atmospherically relevant aging processes, *Environ. Sci. Technol.* 49 (2015) 2806-2814.
- [4] S. Maji, S. Ahmed, W.A. Siddiqui, S. Aggarwal, A. Kumar, Impact of Di-methyl Ether (DME) as an Additive Fuel for Compression Ignition Engine in Reduction of Urban Air Pollution, *Am. J. Environ. Prot.* 3 (2015) 48-52.
- [5] H. Wang, Formation of nascent soot and other condensed-phase materials in flames, *Proceed. Combust. Inst.* 33 (2011) 41-67.
- [6] Y. An, M. Jaasim, V. Raman, H.G. Im, B. Johansson, In-Cylinder combustion and soot evolution in the transition from conventional compression ignition (CI) mode to partially premixed combustion mode, *Energ. Fuel* 32 (2018) 2306-2320.
- [7] P. Liu, Z. Li, W.L. Roberts, The growth of PAHs and soot in the post-flame region, *Proc. Combust. Inst.* (2018), doi: 10.1016/j.proci.2018.05.047.
- [8] P. Liu, Z. He, G.-L. Hou, B. Guan, H. Lin, Z. Huang, The diagnostics of laser-induced fluorescence (LIF) spectra of PAHs in flame with TD-DFT: special focus on five-membered ring, *J. Phys. Chem. A* 119 (2015) 13009-13017.
- [9] P. Liu, H. Lin, Y. Yang, C. Shao, C. Gu, Z. Huang, New insights into thermal decomposition of polycyclic aromatic hydrocarbon oxyradicals, *J. Phys. Chem. A* 118 (2014) 11337-11345.
- [10] H.F. Calcote, D.M. Manos, Effect of molecular structure on incipient soot formation, *Combust. Flame* 49 (1983) 289-304.
- [11] C.S. McEnally, L.D. Pfefferle, Sooting tendencies of oxygenated hydrocarbons in laboratory-scale flames, *Environ. Sci. Technol.* 45 (2011) 2498-2503.
- [12] Y. Zhang, L. Wang, P. Liu, B. Guan, H. Ni, Z. Huang, H. Lin, Experimental and kinetic study of the effects of CO₂ and H₂O addition on PAH formation in laminar premixed C₂H₄/O₂/Ar flames, *Combust. Flame* 192 (2018) 439-451.
- [13] C.S. McEnally, L.D. Pfefferle, Sooting tendencies of nonvolatile aromatic hydrocarbons, *Proc. Combust. Inst.* 32 (2009) 673-679.
- [14] Y. An, S. Teng, Y. Pei, J. Qin, X. Li, H. Zhao, An experimental study of polycyclic aromatic hydrocarbons and soot emissions from a GDI engine fueled with commercial gasoline, *Fuel* 164 (2016) 160-171.
- [15] M. Kashif, J. Bonnetty, A. Matynia, P. Da Costa, G. Legros, Sooting propensities of some gasoline surrogate fuels: Combined effects of fuel blending and air vitiation, *Combust. Flame* 162 (2015) 1840-1847.

- [16] R. Lemaire, D. Lapalme, P. Seers, Analysis of the sooting propensity of C-4 and C-5 oxygenates: Comparison of sooting indexes issued from laser-based experiments and group additivity approaches, *Combust. Flame* 162 (2015) 3140-3155.
- [17] C. McEnally, L. Pfefferle, Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways, *Combust. Flame* 148 (2007) 210-222.
- [18] P.H. Joo, Y. Wang, A. Raj, S.H. Chung, Sooting limit in counterflow diffusion flames of ethylene/propane fuels and implication to threshold soot index, *Proceed. Combust. Inst.* 34 (2013) 1803-1809.
- [19] Y. Wang, S.H. Chung, Effect of strain rate on sooting limits in counterflow diffusion flames of gaseous hydrocarbon fuels: Sooting temperature index and sooting sensitivity index, *Combust. Flame* 161 (2014) 1224-1234.
- [20] C. Arcoumanis, C. Bae, R. Crookes, E. Kinoshita, The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review, *Fuel* 87 (2008) 1014-1030.
- [21] S.H. Park, C.S. Lee, Applicability of dimethyl ether (DME) in a compression ignition engine as an alternative fuel, *Energy Conversion and Management* 86 (2014) 848-863.
- [22] M. Sirignano, M. Salamanca, A. D'Anna, The role of dimethyl ether as substituent to ethylene on particulate formation in premixed and counter-flow diffusion flames, *Fuel* 126 (2014) 256-262.
- [23] J. Wu, K.H. Song, T. Litzinger, S.-Y. Lee, R. Santoro, M. Linevsky, Reduction of Pah and Soot in Premixed Ethylene-Air Flames by Addition of Dimethyl Ether, *Combust. Sci. Technol.* 178 (2006) 837-863.
- [24] S.S. Yoon, D.H. Anh, S.H. Chung, Synergistic effect of mixing dimethyl ether with methane, ethane, propane, and ethylene fuels on polycyclic aromatic hydrocarbon and soot formation, *Combust. Flame* 154 (2008) 368-377.
- [25] R.J. Varghese, V.R. Kishore, M. Akram, Y. Yoon, S. Kumar, Burning velocities of DME(dimethyl ether)-air premixed flames at elevated temperatures, *Energy* 126 (2017) 34-41.
- [26] H. Wu, Z. Shi, C.-f. Lee, H. Zhang, Y. Xu, Experimental and kinetic study on ignition of DME/ n -butane mixtures under high pressures on a rapid compression machine, *Fuel* 225 (2018) 35-46.
- [27] S.C. Sorenson, Dimethyl Ether in Diesel Engines: Progress and Perspectives, *J. Eng. Gas Turb. Power* 123 (2001) 652.
- [28] X.L. Zheng, T.F. Lu, C.K. Law, C.K. Westbrook, H.J. Curran, Experimental and computational study of nonpremixed ignition of dimethyl ether in counterflow, *Proc. Combust. Inst.* 30 (2005) 1101-1109.
- [29] M. Zeng, J. Wullenkord, I. Graf, K. Kohse-Höinghaus, Influence of dimethyl ether and diethyl ether addition on the flame structure and pollutant formation in premixed iso -octane flames, *Combust. Flame* 184 (2017) 41-54.
- [30] C.S. McEnally, L.D. Pfefferle, The effects of dimethyl ether and ethanol on benzene and soot formation in ethylene nonpremixed flames, *Proc. Combust. Inst.* 31 (2007) 603-610.
- [31] A.E. Karataş, Ö.L. Gülder, Soot formation in high pressure laminar diffusion flames, *Prog. Energ. Combust.* 38 (2012) 818-845.

- [32] H. Bohm, H. Bohm, H. Jander, B. Luers, J. Pietscher, H.G. Wagner, M. Weiss, The influence of pressure and temperature on soot, *Proc. Combust. Inst.* 22 (1988) 403-411.
- [33] H.M.F. Amin, W.L. Roberts, Soot measurements by two angle scattering and extinction in an N₂-diluted ethylene/air counterflow diffusion flame from 2 to 5 atm, *Proc. Combust. Inst.* 36 (2017) 861-869.
- [34] C.J. Sung, B. Li, H. Wang, C.K. Law, Structure and sooting limits in counterflow methane-air and propane-air diffusion flames from 1 to 5 atmospheres, *Proc. Combust. Inst.* 27 (1998) 1523-1529.
- [35] F. Fuest, R.S. Barlow, J.-Y. Chen, A. Dreizler, Raman/Rayleigh scattering and CO-LIF measurements in laminar and turbulent jet flames of dimethyl ether, *Combust. Flame* 159 (2012) 2533-2562.
- [36] Chemkin Pro: a chemical kinetics package for the analysis of gas-phase chemical kinetics, Reaction Desig. Release 15112 (2011).
- [37] Y. Wang, A. Raj, S.H. Chung, S. Mani Sarathy, A PAH growth mechanism and effect of alcohol addition on PAH formation in counterflow ethylene diffusion flames, *Proc. Eur. Combust. Meeting* (2015).
- [38] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, A Hierarchical and Comparative Kinetic Modeling Study of C1–C2 Hydrocarbon and Oxygenated Fuels, *Intl. J. Chem. Kinet.* 45 (2013) 638-675.
- [39] P. Liu, Y. Zhang, L. Wang, B. Tian, B. Guan, D. Han, Z. Huang, H. Lin, Chemical mechanism of exhaust gas recirculation on polycyclic aromatic hydrocarbons formation based on laser-induced fluorescence measurement, *Energ. Fuel* 32 (2018) 7112-7124.
- [40] P. Liu, H. Lin, Y. Yang, C. Shao, B. Guan, Z. Huang, Investigating the Role of CH₂ Radicals in the HACA Mechanism, *J. Phys. Chem. A* 119 (2015) 3261-3268.
- [41] K.T. Kang, J.Y. Hwang, S.H. Chung, W. Lee, Soot zone structure and sooting limit in diffusion flames: Comparison of counterflow and co-flow flames, *Combust. Flame* 109 (1997) 266-281.
- [42] W. Wu, A. Adeosun, R.L. Axelbaum, A new method of flame temperature measurement utilizing the acoustic emissions from laser-induced plasmas. *Proc. Combust. Inst.* (2018) doi.org/10.1016/j.proci.2018.07.096.
- [43] N. Peters, *Turbulent Combustion*, Cambridge University Press, Cambridge, U.K., 2000.
- [44] A. Naseri, A. Veshkini, M.J. Thomson, Detailed modeling of CO₂ addition effects on the evolution of soot particle size distribution functions in premixed laminar ethylene flames, *Combust. Flame* 183 (2017) 75-87.
- [45] J. Appel, H. Bockhorn, M. Frenklach, Kinetic Modeling of Soot Formation with Detailed Chemistry and Physics: Laminar Premixed flames of C2 hydrocarbons, *Combust. Flame* 121 (2000) 122-136.
- [46] P.R. Lindstedt, *Soot Formation in Combustion* (H. Bockhorn Eds.), Springer-Verlag, Berlin, 1994, pp. 417–441.
- [47] C. Shao, B. Guan, B. Lin, H. Gu, C. Gu, Z. Li, H. Lin, Z. Huang, Effect of methane doping on nascent soot formation in ethylene-based laminar premixed flames, *Fuel* 186 (2016) 422-429.
- [48] C. Gu, H. Lin, J. Camacho, B. Lin, C. Shao, R. Li, H. Gu, B. Guan, Z. Huang, H. Wang, Particle size distribution of nascent soot in lightly and heavily sooting premixed ethylene flames, *Combust. Flame* 165 (2016) 177-187.