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An experimental and numerical study of the effects of dimethyl ether addition to fuel on polycyclic aromatic hydrocarbon and soot formation in laminar coflow ethylene/air diffusion flames

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ABSTRACT

The effects of dimethyl ether addition to fuel on the formation of polycyclic aromatic hydrocarbons and soot were investigated experimentally and numerically in a laminar coflow ethylene diffusion flame at atmospheric pressure. The relative concentrations of polycyclic aromatic hydrocarbon species and the relative soot volume fractions were measured using planar laser-induced fluorescence and two-dimensional laser-induced incandescence techniques, respectively. Experiments were conducted over the entire range of dimethyl ether addition from pure ethylene to pure dimethyl ether in the fuel stream. The total carbon mass flow rate was maintained constant when the fraction of DME in the fuel stream was varied. Numerical calculations of nine diffusion flames of different dimethyl ether fractions in the fuel stream were performed using a detailed reaction mechanism consisting of 151 species and 785 reactions and a sectional soot model including soot radiation, inception of nascent soot particle due to collision of two pyrene molecules, heterogeneous surface growth and oxidation following the hydrogen abstraction acetylene addition mechanism, soot particle coagulation, and PAH surface condensation. The addition of a relatively small amount of dimethyl ether to ethylene was found experimentally to increase the concentrations of both polycyclic aromatic hydrocarbons and soot. The synergistic effect on polycyclic aromatic hydrocarbons persists over a wider range of dimethyl ether addition. The numerical results reproduce the synergistic effects of dimethyl ether addition to ethylene on both polycyclic aromatic hydrocarbons and soot, though the magnitude of soot volume fraction overshoot and the range of dimethyl ether addition associated with the synergistic effect of soot are less than those observed in the experiment. The synergistic effects of dimethyl ether addition to ethylene on many hydrocarbon species, including polycyclic aromatic ones, and soot can be fundamentally traced to the enhanced methyl concentration with the addition of dimethyl ether to ethylene. Contrary to previous findings, the pathways responsible for the synergistic effects of benzene, polycyclic aromatic hydrocarbons, and soot in the ethylene/dimethyl ether system are found to be primarily due to the cyclization of l-C_6H_6 and n-C_6H_7 and to a much lesser degree due to the interaction between C2 and C4 species for benzene formation, rather than the propargyl self-combination reaction route, though it is indeed the most important reaction for the formation of benzene.

1. Introduction

Soot emitted from flames and various combustion devices have been identified to have an adverse health effect on humans [1] and also to be a major contributor to climate change [2]. Significant research attention has been paid in the last four decades to search for various strategies to control soot formation. One of such strategies is to blend the primary hydrocarbon fuel with an additive, which can be either chemically inert or active, to alter the sooting characteristics of the primary fuel. To understand the effects of temperature and the C/H ratio on the tendency to soot in laminar diffusion flames, Schug et al. [3] systematically investigated the sooting heights of laminar coflow ethylene/air diffusion flames under the effect of various additives, of flames fueled by other hydrocarbons, and of flames fueled by acetylene–fuel mixtures. Work on the influence of additives on soot formation conducted up to 1980 was summarized in the review of Haynes and Wagner [4]. Besides the purpose of soot formation control, study of the effect of certain hydrocarbon additives, such as acetylene and benzene, on soot formation also serves as a powerful means to probe the reaction pathways leading to the incipient ring formation

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and nascent soot particles and/or to clarify the relative roles of different pathways to the formation of polycyclic aromatic hydrocarbon (PAH) and soot [5–7].

Soot formation is a very complex phenomenon. Although significant progress has been achieved in the last few decades towards the main chemical species and detailed reaction pathways responsible for the formation of PAHs, nascent soot particles, and their subsequent surface growth processes, certain key steps in the process from gaseous species to the formation of PAH and solid soot particles remain relatively poorly understood [8]. An excellent discussion of the gas-phase chemistry leading to soot formation has recently been provided by Miller et al. [9]. It is important to notice that the following major steps in the process of soot formation have been widely accepted [8]: (i) formation of molecular precursors of soot, (ii) inception of particles from heavy PAH molecules, (iii) mass growth of particles by addition of gas phase molecules, (iv) particle coagulation via collisions, (v) carbonization of particulate material, and (vi) oxidation. Correspondingly, continuous efforts have been made to develop generic soot models applicable to different flames, such as premixed, non-premixed, or fueled by different hydrocarbons, oxygenated fuels, or blended fuels.

The drive towards gaining improved fundamental understanding of the effect of fuel molecular structure on soot formation and searching for effective additives for soot formation suppression in hydrocarbon combustion has generated considerable interest in recent years in the effects of adding oxygenated fuels to conventional hydrocarbon fuels on soot formation. Oxygenated fuels are in general very clean in terms of soot formation and their decomposition species can influence PAH and soot formation in a rather complex way. Two oxygenated fuels of particular interest are dimethyl ether (DME: CH_3–O–CH_3) and its isomer ethanol (EtOH: CH_3–CH_2–OH). These two fuels can be mass produced economically and have been proposed as possible soot reduction additives to conventional hydrocarbons and as alternative fuels (DME to diesel engines and EtOH to gasoline engines). A great deal of research has been conducted to investigate the effects of DME or EtOH addition to the combustion and emission characteristics of engines.

The present study concerns the effects of DME addition to fuel on PAH and soot formation in laminar coflow ethylene/air diffusion flame. Ethylene was chosen as the fuel in this study for the following reasons. First, ethylene is an important intermediate with significant concentrations in the decomposition of larger hydrocarbons [10] and its detailed reaction mechanism is an essential sub-set for the development of combustion mechanisms of higher-order hydrocarbon fuels, such as propane, butane, heptanes, and jet-A. Secondly, ethylene is an interesting hydrocarbon fuel that has been shown to display the synergistic effect in terms of soot formation with the addition of a small amount of propane [11,12] or DME [13,14]. Thirdly, laminar coflow ethylene/air diffusion flames have been extensively investigated experimentally, e.g. [15–17], and there exists a quite comprehensive dataset of temperature and soot volume fraction distributions [15–17] that can be used to validate the numerical results for the base case (without DME addition) of this study.

So far there have been only four studies published in the open literature to investigate the effects of DME addition to fuel on PAH and soot formation in laminar ethylene flames [10,13,14,18]. Wu et al. [10] conducted an experimental and computational study of the effects of DME addition on PAH and soot formation in rich premixed ethylene/air flat flames established in a McKenna burner. Experimentally, they observed a reduction in PAHs and soot concentrations when a small amount of DME (up to 10% oxygen by weight in the fuel) was added. They also conducted numerical calculations using the PREMIX flame code along the centerline of the flame with a specified temperature profile based on experimental measurements. The reaction mechanism used in their calculations consists of 248 species and 1008 reactions. Soot was also calculated in a post-processing fashion using a model based on the studies of Wang and Frenklach [19] and Appel et al. [20]. Based on the numerical results they explained the decreased PAH and soot concentrations with the addition of DME mainly by the increased concentrations of O and OH radicals and reduced amount of carbon available for the formation of precursor species. McEnally and Pfefferle [14] conducted an experimental study of the effects of adding a relatively small amount of DME or EtOH to fuel (up to 10% as measured by the volumetric flowrate ratio of DME or EtOH to ethylene) on benzene and soot formation in laminar coflow ethylene/air non-premixed flames. Their experimental results indicate that addition of both DME and EtOH increased the maximum benzene concentration and the soot volume fraction with the effect of DME being somewhat stronger, which is unexpected given the fact that both DME and EtOH produce very little soot. It is interesting to observe that McEnally and Pfefferle [14] (conducted in laminar diffusion flames) and Wu et al. [10] (conducted in laminar premixed flames) obtained opposite trends with regard to the effect of DME addition to ethylene on PAH and soot formation. The fundamental reason for the synergistic effects in ethylene non-premixed flames is that pyrolysis of ethylene produces virtually no odd-carbon species. However, oxidative pyrolysis of ethylene does produce odd-carbon species through reactions such as $C_2H_4 + O = CH_3 + HCO$, where the stability of the carbonyl bond provides a driving force to break the C═C bond. This is demonstrated by the observation of a similar synergistic effect when air is added to the fuel in ethylene non-premixed flames [21,22]. Thus, it is not surprising that synergistic effects from DME addition are observed in non-premixed ethylene flames but not in premixed flames. McEnally and Pfefferle [14] explained the enhanced formation of PAH and soot by the addition of a small amount of DME or EtOH to ethylene in terms of the enhanced concentrations of methyl radical (CH_3) from the decomposition of these oxygenates. The enhanced methyl radical concentrations then prompt the formation of propargyl radical (C_3H_3) through C1 + C2 addition reactions. The increased propargyl radical concentrations then lead to higher benzene concentrations through propargyl self-reaction, which has been identified to be the most important benzene formation reaction, e.g. [13,18]. The greater effect of DME addition on PAH and soot formation than EtOH can be attributed to the higher methyl radical concentrations from its decomposition [14,18]. Yoon et al. [13] experimentally investigated the effects of mixing DME with methane, ethane, propane, and ethylene on PAH and soot formation in laminar counterflow diffusion flames. The relative soot volume fractions and PAH concentrations were measured by planar laser-induced incandescence (LII) and laser-induced fluorescence (LIF) techniques, respectively. They also conducted numerical calculations of the flames using a reaction mechanism consisting of 115 species and 602 reactions steps. However, soot was not included in the numerical calculations. Their experimental results of both PAH concentration and soot volume fraction demonstrate that only the ethylene flames exhibit the synergistic effect, i.e., mixing a small amount of DME to ethylene causes the PAH concentration and soot volume fraction to increase beyond the pure ethylene case, but not the other three hydrocarbon flames. The findings of Yoon et al. with regard to the effects of DME addition to ethylene on PAH concentration and soot formation are in qualitative agreement with those of McEnally and Pfefferle [14]. It is important to notice that the synergistic effect for the PAH concentration persists over a much wider range of DME percentage in the fuel than that for the soot volume fraction (50% vs. 22% of DME in fuel). Yoon et al. [13] also explained the enhanced formation of PAH and soot with the addition of a relatively small amount of DME to ethylene by the enhanced methyl radical concentrations from the decomposition of DME, which then prompt propargyl radical formation and