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Effects of oxygen-enrichment and fuel unsaturation on soot and NO_x emissions in ethylene, propane, and propene flames

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ABSTRACT

We have performed a computational study on the effects of oxygen enrichment[1] and fuel unsaturation on the flame structure, PAHs, soot, and NO_x emissions. Counterflow flames burning ethylene, propane, and propene are simulated with CHEMKIN-Pro, using a validated mechanism with 197 species and around 5000 reactions. The stoichiometric mixture fraction (ζ_{st}) is varied by simultaneously using O_2-enriched airstream and N_2-diluted fuel stream such that the adiabatic flame temperature is nearly constant. Dominant reaction paths are analyzed to examine the relative roles of hydrodynamics and changes in flame structure on PAHs and soot emissions. As ζ_{st} is increased, results indicate a significant reduction in acetylene and PAHs formation, and with additional soot oxidation in the post flame region, it leads to a nearly non-sooting flame. The drastic reduction in PAHs and soot formation can be attributed to both the hydrodynamic and the flame structure effects. At moderate oxygenation levels, changes in flame structure seems to play a more prominent role, while at higher oxygenation levels, the hydrodynamic effect seems to be more important. With the increase in ζ_{st}, the O, OH, and H radical pool is enhanced, and, consequently, the intermediate species (propargyl, allene, and propyne) are reduced to smaller hydrocarbons, decreasing the formation of PAHs and soot. With further increase in ζ_{st}, the flame location shifts from oxidizer to fuel side, and, consequently, PAH species and soot get oxidized in the oxygen rich region, leading to nearly soot free flames. However, as ζ_{st} is increased, NO emissions increase monotonically. At low ζ_{st} values, the prompt route contributes more to NO formation, while at high ζ_{st} values, the thermal route contributes more. The rate of production analysis indicates that the presence of double bond promotes reactions which produce higher amounts of allyl and propargyl species, and thus higher amounts of soot precursors; benzene and pyrene. Consequently, propene and ethylene flames produce significantly higher amount of soot compared to propane flames.

1. Introduction

PM (particulate matter) emissions from the combustion of fossil fuels represent a major health and environment concern. Fine particles, especially 10 μm and smaller (PM10) get trapped in the respiratory tract, while finer particles (PM2.5) can penetrate deep into lungs and subsequently into blood stream, causing serious health problems, including cardiovascular and lung diseases [1,2]. Such particles are also known to contribute to global warming [1] and adversely affect our aquatic and terrestrial ecosystems. In particular, as reported by Hansen and Nazarenko, the efficacy of soot climate forcing is twice that of CO_2 [2]. As a consequence, the emission regulations have become increasingly stringent over the years, and soot production in flames continues to be an important area of research.

Soot formation represents a complex phenomenon involving many physical and chemical processes [3]. Various processes include pyrolysis and formation of smaller hydrocarbons, such as acetylene and propargyl, followed by the formation and growth of polycyclic aromatic hydrocarbon (PAH) species, nucleation, growth of particle size and mass through surface reactions, PAH condensation, particle agglomeration and coagulation, and finally soot oxidation. There has been extensive research dealing with these processes. This research has identified a number of important parameters affecting soot emission. Essentially, the amount of soot produced is found to be strongly influenced by the fuel structure [4–7], flame temperature and structure [8–11], residence time [4,8,12], and compositions of fuel and oxidizer streams [13–19].

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[1] In this paper, the term oxygen enrichment (or oxygenation) is used to indicate simultaneous O_2 enhancement of the oxidizer stream and N_2 dilution of the fuel stream.

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Many fundamental studies have considered laminar nonpremixed and partially premixed flames in a counterflow configuration, which provides nearly 1-D flow field, and thus facilitates well-resolved measurements and simulations. Results from such studies are also relevant to turbulent flames in the context of laminar flamelet modeling.

Previous research on soot emissions has also identified new combustion technologies for reducing NO_x and soot emissions from various combustion systems. These include high temperature air combustion (HiTAC) [20], flameless combustion [21,22], mild combustion [23], low temperature combustion [24] and oxygen-enhanced combustion [25]. One effective approach of employing oxygen-enhanced combustion (OEC) for soot reduction in nonpremixed flames is to use the oxygen enrichment of air stream along with the nitrogen dilution of fuel stream. As discussed by Du and Axelbaum [13] and Skeen et al. [14], this alters the stoichiometric mixture fraction (ζ_{st}), while keeping the flame temperature nearly the same, and can significantly affect on the flame structure and soot formation. Skeen et al. [14] demonstrated the effectiveness of this approach and reported a dramatic reduction in the concentration of PAH species (i.e., benzene and phenyl) in ethylene counterflow flames. They postulated that the formation of soot precursors is inhibited due to the prominent changes in the flame structure, which makes the H abstraction reactions very active in soot forming regions, thus decreasing the rate of production of soot precursors.

The literature review indicates that most previous studies dealing with nonpremxied flames have considered either fuel stream dilution [8,9,11,13–15] or oxidizer stream dilution/enrichment [11,18,25,26] on PAH and soot emissions. As noted earlier, Skeen et al. [14] used simultaneously the oxygen enrichment of air stream and nitrogen dilution of fuel stream, and examined its effect on the formation of PAH species. The present study utilizes a similar approach for modifying the flame structure, and characterizes its effect on NO_x, PAH and soot emissions. The paper has two major objectives. One is to examine comprehensively the effect of altering ζ_{st} on NO_x, PAH and soot emissions in nonpremixed flames. Previous researchers have demonstrated that by sufficiently increasing ζ_{st}, one can obtain nearly soot-free diffusion flames. They attributed this soot-inhibiting phenomenon to either hydrodynamics [27,28] or flame structure effect [14,29]. The present study examines both of these effects by analyzing the detailed flame structure and the dominant reaction paths at different ζ_{st}. Moreover, previous computational studies have considered the effect of ζ_{st} on the formation of PAH species, while the present study examines its effect on NO_x, PAH and soot emissions. In the context of hydrodynamic effect, it is important to consider soot emission, since soot oxidation plays a key role. Another objective is to characterize the effect of unsaturation on NO_x, PAH and soot formation. Thus simulations are performed for counterflow flames burning small hydrocarbon fuels, namely, ethylene, propane and propene. For all three fuels, major routes for the formation of soot precursors are also identified. Ethylene is chosen since it has been identified as an important species in the combustion of larger hydrocarbons, and also plays a significant role in the PAH and soot formation. In addition, propane and propene are used to characterize the effect of unsaturation in smaller hydrocarbons on emissions. Most previous studies dealing with fuel unsaturation have considered larger hydrocarbons [5–7]. While there has been some work concerning smaller biodiesel surrogates, such as methyl butanoate, the focus has been mainly on the development of kinetic models [30–32].

2. Numerical model

Simulations are performed using OPPDIF in the CHEMKIN-Pro package [33] in an opposed-jet configuration, shown schematically in Fig. 1. It consists of two opposing jets that are being issued from two coaxial nozzles. The distance between the nozzles is 20 mm, and the inlet temperatures of both fuel and air jets are maintained at 300 K. A diffusion flame is established by specifying a global strain rate [34], expressed as:

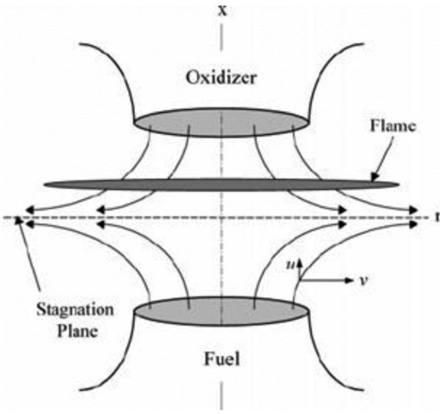

Fig. 1. Schematic of counterflow configuration used for establishing diffusion flames.

$$a_G = \frac{2v_o}{L}\left(1 + \frac{v_f}{v_o}\frac{\sqrt{\rho_f}}{\sqrt{\rho_o}}\right) \tag{1}$$

Here L is the distance between the nozzles, v and ρ the inlet velocity and density, respectively, and the subscripts f and o represent fuel and oxidizer streams, respectively. A global strain rate of $a_G = 100\ s^{-1}$ is used in the present study. The velocities at the fuel and oxidizer inlets are specified by equating the momenta of the two streams for a given a_G. The grid independence was achieved by using successively finer grids and varying the GRAD and CURV parameters so that the solution is nearly independent of the grid system.

Detailed models are employed to compute the flame structure, NO_x and soot emissions. The soot processes considered include nucleation, surface growth, coagulation, and oxidation. The soot model is combined with a detailed fuel oxidation and NO_x chemistry model [17] involving 198 species and 4932 reactions, with coronene ($C_{24}H_{12}$) being the largest species. The NO_x mechanism includes the thermal NO, prompt NO, intermediate N_2O, and intermediate NNH routes. Details of these routes including relevant reactions have been provided in a previous investigation [44]. Soot modeling has been particularly challenging as it involves a number of complex physical and chemical processes. However, significant progress has been reported in this regard [35–39]. Soot formation process in the current study involves formation of nuclei through nucleation and polymerization of a primary particle, which subsequently grows through coagulation and surface reactions, while also undergoing oxidation. The nucleation reaction which defines the particle size and surface coverage is considered to be irreversible, and based on pyrene ($C_{16}H_{10}$) recombination reaction, which forms one soot nucleus with 32C atoms, as indicated by Eq. (2). The nuclei formed interact with each other through coagulation as well as with gaseous species on its surface, whose dynamics is modeled by solving particle size distribution functions (PSDFs) using method of moments approach developed by Frenklach et al. [39,40]. This approach is computationally economical, while modeling soot processes in sufficient detail, and thus providing overall/average soot properties, such as average particle size, soot volume fraction and number density, using the particle size moments. Further the surface growth includes coagulation and surface reactions, which are defined through the HACA mechanism [38]. The soot oxidation reaction is represented by Eq. (7), while