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Numerical study of the effects of pressure on soot formation in laminar coflow n-heptane/air diffusion flames between 1 to 10 atm

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Abstract:

Laminar nitrogen-diluted n-heptane diffusion flames burning in coflow air were numerically simulated at pressures from 1 to 10 atm. Numerical simulations were performed by using a detailed reaction mechanism containing 175 species and 1086 reactions with PAH formation up to pyrene and a sectional soot model. The soot model consists of inception as a result of the collision of two pyrene molecules, heterogeneous surface growth and oxidation following the hydrogen abstraction acetylene addition (HACA) mechanism, and soot particle coagulation and PAH surface condensation. Comparisons with available experimental data indicate that the numerical model reproduces successfully the influence of pressure on the flame structure and soot production. All the soot formation processes are enhanced with increasing pressure and HACA dominates the soot mass growth over the pressure range considered. PAH condensation is the most sensitive process to pressure whereas the inception and HACA processes exhibit similar pressure dependency. These trends are directly related to the pressure dependence of the molar concentrations of the species involved in soot formation. The increase in the molar concentrations of benzene and pyrene with pressure results from both physical and chemical effects. Propargyl recombination and interconversion of phenyl to benzene dominate the formation of benzene low in the flame over the pressure range considered, though the contributions of the addition of acetylene to n-butadienyl radical increases significantly with pressure in the flame centerline region.

Key Words: Laminar diffusion flame, n-heptane, soot production, high pressure, PAH-based soot model.

1. Introduction

Understanding the influence of pressure on soot formation is of great practical and fundamental interest since many combustion systems, such as aircraft gas turbines and diesel engines, operate at elevated pressures for reasons of optimal efficiency and size and our current understanding of soot formation at elevated pressures is still quite limited, though rapid progress has been made in recent years. The environmental and health impact of soot are also important factors to conduct soot research, since combustion generated soot emissions have been found detrimental to human health and suggested to be the second largest contributor to climate change after CO₂.

Although turbulent combustion occurs in practical combustion systems, it is important to conduct experimental studies of soot at elevated pressure in laminar diffusion flames to avoid the difficulties inherent to turbulence and to gain fundamental insights into the effect of pressure and fuel chemistry on soot formation. The experimental works carried out in high pressure laminar coflow diffusion flames were recently reviewed [1]. Flower and Bowman [2] found that the maximum line-of-sight integrated soot volume fraction in ethylene/air coflow diffusion flames at pressure from 1 to 10 atm was proportional to the pressure, P , raised to an exponent of about 1.2. McCrain and Roberts [3] found that the flame-diameter-integrated soot volume fraction scales with $P^{1.0}$ and $P^{1.2}$ in laminar coflow methane/air and ethylene/air diffusion flames, respectively, in their experimental study at elevated pressures up to 25 atm. The most recent experimental studies were based on the analysis that, in buoyancy-dominated laminar coflow diffusion flames, flame heights and residence times are independent of pressure if the fuel mass flow rate remains fixed. This implies that measurements can be directly compared at the same heights above the burner [1]. These studies have considered methane [4, 5], ethane [6], ethylene [7], propane [8] and n-heptane [9]. In particular it was found

that, when a relevant normalization for soot yield and pressure is considered, soot yield exhibits a unified dependence on pressure for methane, ethane and propane [10].

Only few numerical studies of soot formation in laminar coflow diffusion flames at elevated pressures were reported and most of them were carried out with semi-empirical acetylene-based soot models [11-14] and only three were conducted using a more detailed soot model [15-17]. These studies concluded that the pressure effects on soot formation is largely due to an enhancement in density [11-17] and increasing pressure enhances the air entrainment into the fuel stream near the burner, accelerating the fuel pyrolysis [12-17]. In addition, they provided fundamental insights in the flame geometry [12,14,16], confirming that, for a fixed fuel mass flow rate, flame height and residence time are almost independent of pressure whereas the flame radius scales with $P^{-1/2}$. Nevertheless, the use of a semi-empirical soot model excludes any direct chemical effects on soot production. Eaves et al. used a detailed PAH-based soot model to investigate the influence of pressure on soot formation in ethane-air coflow diffusion flames [15,16]. They found that soot formation is dominated by surface growth along the flame wings whereas PAH condensation prevails along the centerline. In addition they demonstrate clearly the strong influence of considering the preheating of the fuel tube [15,16]. Guo et al. [17] also used a detailed PAH-based soot model and showed that soot formation is dominated by the H-abstraction acetylene-addition (HACA) process at atmospheric pressure whereas the PAH condensation prevails at higher pressures. They showed also that the chemical pathways leading to the formation of benzene are modified when the pressure increases.

The previous numerical studies of soot formation at elevated pressures were limited to common gaseous fuels such as methane or ethylene and no such numerical investigations have been carried out in laminar coflow diffusion flames of liquid fuels. The objective of this study is to investigate numerically the sooting behavior of a laminar coflow nitrogen diluted n-heptane/air diffusion flame with increasing pressure from 1 to 10 atm. Numerical results are compared with the experimental

data of Karataş et al. [9]. The motivation of this study is twofold. First, n-heptane is of particular interest since it is one of the primary constituents in surrogate fuels of gasoline [18]. Second, the laminar coflow n-heptane/air diffusion flame of Karataş et al. [9] is the only liquid fuel flame that has been recently experimentally investigated at elevated pressures.

2. Numerical Model

2.1. Governing equations and solution method

The governing equations and the solution method have been described in previous studies [19-21] and will be described briefly. The numerical model includes the solution of the overall continuity equation, the Navier–Stokes equations in the low Mach number formulation, and transport equations for gas-phase species mass fraction and energy. A sectional method is used to describe the soot particle dynamics, leading to resolution of additional transport equations for sectional soot aggregate and primary particle number densities [19,21].

The conservation equations are solved in axisymmetric cylindrical coordinates using a finite volume method and the SIMPLE algorithm. Details of the discretization method and the strategy for handling the stiffness of the equation system can be found in previous publications [12,17,19,20,21]. Because the solution of such a large highly non-linear partial differential equation system is very computationally demanding, parallel computation with a domain decomposition method was employed as described in [21]. The radiative source term in the energy conservation equation was included and computed by the discrete ordinate method coupled to a statistical narrow-band-correlated K (SNBCK)-based [22].

2.2. Soot model

The fixed sectional soot model used in this study has been employed and described in several previous studies [19-21]. The range of soot aggregate mass is divided into a number of discrete sections. In each section, all the soot aggregates are assumed to be identical and to be comprised of equally sized spherical primary particles and to have a constant fractal dimension of 1.8. The evolution of each section is governed by two transport equations for the number densities of soot aggregate and primary particles [19,22]. The incipient soot particles are assumed to be spherical and belong to the first section. Further details can be found in [19-21].

Coagulation terms are calculated using the same method given in [23]. The collision kernel of two aggregates in the entire Knudsen number regime is calculated based on [24]. It is noted that this method assumes unity coagulation efficiency, i.e., once two aggregates collide they stick together. The soot kinetics model is based on the work of Appel et al. [25]. Although in reality soot inception is the result of collisions of various large PAHs, for simplicity soot inception is assumed to be the result of collision of two pyrene molecules (A4). Surface growth and oxidation are assumed to follow the HACA mechanism by using the same parameters as in [25], except the steric factor α which is taken to be 0.25 in this study. PAH surface condensation accounts for the growth of soot particles due to the condensation of A4 molecules colliding with soot aggregates on their surface [25]. The condensation rate is calculated by the collision theory between A4 molecules and aggregates [23]. Since not all collisions lead to successful condensation, a PAH condensation efficiency is introduced and assumed to be 0.5 [19].

2.3. Chemical mechanism

The reaction mechanism is a shortened version of that developed recently by Raj et al. for gasoline surrogate fuel involving mixtures of n-heptane, iso-octane and toluene [26]. The mechanism of Raj et al. consists of 231 species and 1500 reactions and was generated from that of Marchal et al. [27], developed also for gasoline surrogate fuel and considering pyrene (A4) as the largest PAH, by

extending it up to coronene (A7) and by adding several new PAH reactions to provide more reliable predictions of the concentrations of large PAHs. In particular these modifications were found to improve considerably the calculated concentrations of pyrene in n-heptane flame [26]. The shortened mechanism consists of 175 chemical species and 1086 reactions. The PAHs beyond A4 in the mechanism of Raj et al. [26] were removed to keep the chemical mechanism consistent with the ABF soot model, which assumes that inception and condensation involve only A4.

2.4. Computational details

The present numerical calculations intend to simulate the experimental work of Karataş et al. [9]. The burner consists of a central fuel tube of 3 mm inner diameter and a co-annular air tube of 25.4 mm inner diameter. Heated nitrogen and n-heptane mixture is delivered through the central tube with flow rates of 1.04 mg/s and 0.49 mg/s, respectively, and the fuel line is maintained at about 520-530 K. Air is delivered through the annular region with a flow rate of 0.42 g/s and the line is maintained at 475 K. Although the visible flame appearance was investigated at 1, 2, 5, 7, and 10 atm, spectral soot emission (SSE) measurements were only conducted at 2, 5, and 7 atm for soot volume fraction and temperature distributions. The SSE technique detects a set of integrated spectral radiation emissions across the flame over a range of wavelength (650-1050nm [9]) to determine radially resolved soot volume fraction and temperature [28]. Under the flame conditions of Karataş et al. [9], the error in soot volume fraction and temperature measurements was estimated to be about 30-40% and up to about 150 K, respectively, based on [28]. The error of temperature grows rapidly towards the outer edge of the flame due to the decrease in soot concentration. In addition, the neglect of self-absorption in the data analysis of Karataş et al. [9] is likely to lead to underestimation of temperature by up to about 60 K [29].

Numerical calculations were performed at 1, 2, 5, 7 and 10 atm according to the experimental conditions of [9] and in a domain of 1.79 cm (z) $\times$ 0.81 cm (r) with 210 (z) $\times$ 88 (r) control volumes.

A non-uniform mesh was used with a resolution of 0.05 mm in the r-direction and 0.066 mm in the z-direction near the burner exit. At the fuel inlet, the fuel/nitrogen mixture was composed of 11.63% of heptane in volume (balanced by nitrogen), the inlet temperature of the fuel stream was set at 525 K and a near flat velocity profile was assumed with a mean stream velocity of $25.616/p$ (p in atm) cm/s. At the air stream, the inlet temperature was set at 475 K and a uniform velocity of $113.09/p$ cm/s was assigned according to the experiments of [9].

3. Results and Discussions

3.1. Flame geometry

Numerical flame heights, h_f , and flame radii, r_f , at a height of 5 mm above the burner exit surface are defined by the locations of the peak temperature along the axis and the r-direction, respectively. Figure 1 shows the evolution of h_f with pressure. The Roper analysis predicts that the present flame heights should be independent of pressure [30]. This trend was observed experimentally despite small deviations attributed to flame instability [9], with a luminous flame height estimated to be about 9.5 mm. It should be noted that experimental flame radii were defined consistently with the numerical results by the temperature peak at a height of 5 mm whereas experimental flame heights were taken from [9] based on luminous flame since temperature along the flame axis were not available in [9].

Figure 1 shows that the calculated flame heights are lower than 9.5 mm at 1 and 2 atm whereas a more satisfactory agreement is observed for higher pressures. In addition, the predicted flame height increases slightly with pressure. This behavior is consistent with previous experimental [6,8] and numerical observations [12,14]. The comparison of the computed flame heights with the experimental ones for ethane and propane, reported in Fig. 1, suggests that the model reproduces quantitatively the evolution of flame height of these flames with pressure. It is noted that Charest et

al. [13] showed numerically that flame heights become effectively independent of pressure when soot and radiation are neglected, i.e., when the assumptions of the Roper theory are satisfied.

Both the computed and experimental flame radii, based on the peak temperature at a height of 5 mm, are also plotted in Fig. 1. As expected, the flame radius decreases with increasing pressure. The predicted flame radii are larger than the experiments and the rate of decrease is underestimated. Theoretical analysis shows that the pressure independence of the flame height implies that the flame radius should scale with $P^{-1/2}$ [1]. For pressures larger than 2 atm, the predicted flame heights are approximately independent of pressure, and the exponent of the pressure dependence of flame radius of -0.38 is close to -1/2. Between 1 and 2 atm, the increase in flame height with pressure is more pronounced and, consistently, a slower rate of decrease is observed for the flame radius.

3.2. Pressure effects on soot production and temperature

Figures 2a, b, and c display the measured and calculated radial profiles of soot volume fraction, f_s , at three heights: low in the flame where soot particles form in the annular region due to nucleation and surface growth ($z = 3$ mm, Fig. 2a), near the middle of the flame where the maximum soot volume fraction occurs ($z = 5$ mm, Fig. 2b), and higher in the flame where soot is oxidized ($z = 7.5$ mm, Fig. 2c). Soot volume fractions at atmospheric pressure are not shown since the computed peak value is very low ($\sim 1 \times 10^{-3}$ ppm). Figures 2a-c show that the model captures the primary features of the experiments, although the predicted radial position of the peak soot volume fraction is shifted outward from the axis compared to the experimental results. The large discrepancies observed at $z = 7.5$ mm at 2 atm can be related to the underestimation of the flame height (see Fig. 1). Based on the findings of previous studies [13-16], the observed discrepancies in flame heights and the radial location of peak soot concentration can be, at least partially, attributed to the neglect of the fuel preheating effect in our modeling. Indeed, for all the pressures considered the flame is close to the fuel tube, especially with increasing pressure. It is also observed in Fig. 2a-c that, as the pressure

increases, the peak of soot volume fraction moves toward the flame centerline and the soot volume fractions increase as a consequence of both flame narrowing and enhancement in soot production.

The predicted and measured temperatures are compared at the three heights in Figs. 2d-f. The calculated temperature peaks are also found to shift outward from the centerline compared to the experiments, confirming that the model overestimates flame radii. As mentioned in section 2.4, the error in the experimental temperatures can be up to about 150 K and is underestimated systematically by about 60 K due to the neglect of self-absorption effect. Therefore, the predicted temperatures are in general within the experimental error of the measured values. At $z = 3$ and 5 mm the experimental temperatures are observed to decrease with increasing pressure as a results of enhancement in radiative loss. This behavior is reproduced by the model although a slower rate of decrease is obtained. Higher in the flame (Fig. 2f) a reduction in temperature of about 200 K is observed as the pressure increases from 1 atm to 10 atm.

Figure 3 shows the evolution of the maximum soot volume fraction, $f_{s,max}$, and the maximum soot conversion factor, $\eta_s(z)$, with pressure. $\eta_s(z)$ is defined as:

$$\eta_s(z) = \frac{2\pi\rho_s \int v_z(r,z)f_s(r,z)rdr}{\dot{m}_c} \quad (1)$$

where $\rho_s = 1.8 \text{ g/cm}^3$, v_z is the axial velocity and $\dot{m}_c$ is the carbon mass flow rate (0.41 mg/s). The calculated magnitude and rate of increase with pressure of both $f_{s,max}$ and $\eta_{s,max}$ compare favorably well with the experimental data of Karataş et al. [9]. Both $f_{s,max}$ and $\eta_{s,max}$ increase rapidly between 1 atm and 2 atm. For higher pressure their rates of increase slow down and $f_{s,max}$ and $\eta_{s,max}$ scale with P^n with $n = 3.24$ and 2.80 (2.37 for the experiments), respectively. It can be pointed out that, for both $f_{s,max}$ and $\eta_{s,max}$, the exponents are higher than those observed for other fuels over the same range of pressures (see Table 1 in [1]). In particular, for propane [8] and ethane [6] flames with the

same carbon mass flow rates as in the present flames, the values of the exponents were found to be 1.4 (propane) and 2.3 (ethane, $2 \leq P \leq 5$ atm) or 1.4 (ethane, $5 \leq P \leq 15$ atm) for $f_{s,max}$ and 1.1 (propane) and 2.2 (ethane, $2 \leq P \leq 5$ atm) or 1.1 (ethane, $5 \leq P \leq 15$ atm) for $\eta_{s,max}$. This suggests that the soot properties are more sensitive to pressure in n-heptane flames.

3.3. Pressure effects on soot production rates

Figure 4a displays the axial distributions of radially-integrated (cross sectional) soot inception, PAH condensation, and HACA surface growth rates at 2, 5, 7 and 10 atm. The onset of soot formation appears to begin earlier as the pressure increases owing to enhanced fuel pyrolysis [12,14]. The surface growth rate by HACA dominates the soot mass growth process over the pressure range considered. Guo et al. [17] predicted different pressure dependence of soot formation processes in axisymmetric ethylene diffusion flames over the same ranges of pressure that the HACA process prevails at atmospheric pressure but PAH condensation becomes dominant from 6 atm. Figure 4a shows also that, at 2 atm, the maximum integrated inception and PAH condensation rates reach similar values. At higher pressures the condensation rate becomes significantly larger. Figure 4b displays the evolution of the normalized maximum rates of the three soot production mechanisms with pressure. These values are computed by dividing the maximum rate by that at 2 atm. All three soot formation rates increase rapidly with pressure between 2 and 5 atm and with a slower rate between 5 and 10 atm. The condensation rate is most sensitive to pressure, which is consistent with the conclusions of Guo et al. [17] for ethylene diffusion flames. On the other hand, inception and HACA rates exhibit similar dependence on pressure. The evolution of these normalized maximum soot rates with pressure follows the same trends as observed in Fig. 4a and thus reveals the influence of pressure on soot formation from a different perspective.

The mechanisms leading to enhanced soot formation with increasing pressure are analyzed at locations where soot formation rates peak. The maximum HACA rate occurs in flame wings whereas

the maximum inception and nucleation rates occur at approximately the same axial location of high A4 concentrations. Temperature is not responsible for the observed increase in normalized soot formation rates since it decreases modestly with pressure, from 2025 K at 2 atm to 1892 K at 10 atm at the positions of the maximum HACA rate and from 1711 K at 2 atm to 1669 K at 10 atm at the positions of the maximum inception and PAH condensation rates. The enhancement in soot formation rates is thus related to the molar concentrations of the species involved in the soot formation processes. Figure 4b displays the normalized molar concentrations of C_2H_2 , H radical, and pyrene. The normalized concentrations are computed in the same manner as the normalized soot formation rates. The normalized concentration of A4 scales with $P^{1.14}$ which explains the increase in inception rate with pressure. The PAH condensation rate depends on both the molar concentration of A4 and the soot particle surface area, with the latter being proportional to $P^{1.86}$ at the locations of maximum PAH condensation rate. Therefore, the pressure dependence of PAH condensation rate is stronger than that of inception rate as shown in Figs. 4a and 4b. The HACA rate depends in a complex manner on the soot surface area, which scales with $P^{3.45}$ at the location of maximum HACA rate, and on the molar concentrations of C_2H_2 and H. In agreement with the conclusions drawn by Guo et al. for ethylene diffusion flames [17], the normalized molar concentration of C_2H_2 increases at a slower rate than that of A4 ($\propto P^{0.65}$) whereas the normalized molar concentration of H decreases as the pressure increases (see Fig. 4b). This is why the HACA rate increases slower with pressure than the PAH condensation rate. The first aromatic ring, A1, plays an important role in the subsequent growth of larger PAHs and soot formation process. Similar to pyrene, the maximum concentrations of A1 also occur in the flame centerline region around $z = 5$ mm. Figure 4b shows that the normalized concentration of A1 is proportional to $P^{1.77}$ and increases faster with pressure than those of C_2H_2 and A4.

The above discussion suggests that the strong increase in soot surface area, A_s , is the dominant factor in the enhancement of HACA and condensation mechanism with pressure, in agreement with the conclusions drawn by Eaves et al. [15,16]. This leads to a positive feedback process where growth

and condensation increase soot surface area, which in turn enhances HACA and condensation processes. An analysis of the results shows that $A_s = N_s \pi D_s^2 / 4$ increases with pressure as a result of an increase in the particle size, D_s , whereas the particle number density, N_s , is reduced. As the pressure increases from 2 atm to 7 atm, N_s and D_s respectively decreases and increases by an order of magnitude, leading to an enhancement in surface area of approximately an order of magnitude. In the absence of chemical effects, the species molar concentrations are expected to scale with P . As a consequence, the previous results show that the chemical effects tend to enhance the formation of A1 and A4 and to reduce the formation of C_2H_2 . The effects of pressure on the chemical pathways leading to the formation of A1 are discussed next.

3.4. Pressure effects on the formation of A1

The computed reaction rates of all the reactions involving A1 were analyzed. It was found that A1 is primarily formed through the following reactions:

Regarding R371, A1- is mainly formed by reactions $C_3H_3 + C_3H_3 = A1- + H$ and $n-C_4H_5 + C_2H_2 = A1-$.

Figure 5a shows the molar concentration of A1, [A1], and the reaction rates, R_i , of the above three reactions along the flame centerline at 2 and 10 atm. At 2 atm, [A1] increases sharply between 0.4 cm and 0.5 cm before being rapidly consumed between 0.5 cm and 0.6 cm. The rapid increase is mainly due to R236 which dominates the production of A1 at 2 atm. The contribution of R371 is also important, especially downstream the peak of [A1], whereas that of R298 is negligible. The reaction rates of all the three reactions are significantly enhanced at 10 atm, leading to a substantial increase in [A1]. [A1] increases rapidly between 0.3 cm and 0.46 cm and a large part of the increase between

0.3 and 0.4 cm is due to R298. Nevertheless, R236 and R371 are the two largest contributors to the production of A1.

The formation of A1 just above the burner rim is of great interest since it is the starting point of the PAH growth sequence and the subsequent inception and growth of soot along the flame wings. Figure 5b displays the evolution of the maximum reaction rates of R236, R298 and R371 along the flame wings as a function of the distance above the burner exit surface. The trends are the same as those observed in Fig. 5a. The formation of A1 is dominated by R236 and R371 at both 2 and 10 atm but the relative contribution of R298 is significantly enhanced with increasing pressure. The results shown in Fig. 5b indicate that the recombination reaction of propargyl, R236, which was found important at atmospheric pressure [20], also contributes the most to A1 formation low in the flame just above the burner rim at elevated pressures.

4. Concluding remarks

Laminar axisymmetric coflow nitrogen-diluted n-heptane/air diffusion flames at pressures between 1 and 10 atm were simulated to gain insights into the influence of pressure on the flame structure and PAH and soot formation. The following conclusions can be drawn:

- 1) The model reproduces reasonably well the experimentally observed influence of pressure on flame geometry and soot production. This constitutes the very first validation study of both the chemical mechanism and soot production model in modelling more complex liquid hydrocarbon fuels at elevated pressures.
- 2) Both model and experimental results suggest that soot properties are more sensitive to pressure in n-heptane diffusion flames than in flames fuelled with common gaseous fuels.
- 3) Over the range of pressure investigated, soot mass growth is dominated by acetylene addition. The rates of all soot formation processes increase with pressures, with the PAH condensation rate being the most sensitive and the inception and HACA rates having similar pressure dependence.

The increase in soot surface area with pressure is the primary factor to the increase in condensation and surface growth rates. It results from an increase in the particle size and leads to a positive feedback between surface growth processes and soot surface area.

- 4) The increase of PAH concentrations with pressure is related to both physical and chemical effects.
- 5) Over the pressure range considered, propargyl recombination and inter-conversion of benzene to phenyl dominate the formation of benzene although the contribution of the addition of acetylene to n-butadienyl radical increases significantly with increasing the pressure.

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List of Figure Captions

Figure 1. Flame heights (square) and radii (triangle) as a function of the pressure. Predictions are represented by open symbols whereas experimental data are represented by filled symbols.

Figure 2. Calculated (line) and measured (open symbols) [9] radial profiles of soot volume fraction and temperature at different heights.

Figure 3. Calculated (open symbols) and measured (filled symbols) [9] maximum soot volume fraction (a) and soot conversion factor (b) as a function of pressure.

Figure 4. (a) Integrated soot formation rates as a function of the height for 2 and 10 atm and (b) evolutions of the normalized maximum soot formation rate and normalized mole concentrations of C_2H_2 , H, A4 and A1 as a function of pressure.

Figure 5. Production of A1 at 2 and 10 atm: (a) Axial molar concentration of A1 and reaction rates, (b) Evolution of the maximum reaction rates on the flame wings.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.