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SOOT FORMATION IN HYDROCARBON/AIR LAMINAR JET DIFFUSION FLAMES

by

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Introduction. Soot processes within hydrocarbon/air diffusion flames are important because they affect the durability and performance of propulsion systems, the hazards of unwanted fires, the pollutant and particulate emissions from combustion processes, and the potential for developing computational combustion. Motivated by these observations, this investigation involved an experimental study of the structure and soot properties of round laminar jet diffusion flames, seeking an improved understanding of soot formation (growth and nucleation) within diffusion flames. The present study extends earlier work in this laboratory concerning laminar smoke points [1] and soot formation in acetylene/air laminar jet diffusion flames [2], emphasizing soot formation in hydrocarbon/air laminar jet diffusion flames for fuels other than acetylene.

Past studies of soot formation are reviewed in Sunderland et al. [2] and references cited therein; these summaries indicated that present understanding of soot formation in diffusion flames is limited. Thus, Sunderland et al. [2] carried out measurements in acetylene/air laminar jet diffusion flames at pressures of 0.12-0.25 atm, emphasizing soot nucleation and growth. In this flame system, acetylene is the dominant gas species in the soot formation region and both nucleation and growth were successfully attributed to first-order reactions of acetylene, with nucleation exhibiting an activation energy of 32 kcal/gmol while growth involved negligible activation energy and a collision efficiency of 0.53%. In addition, soot growth in the acetylene diffusion flames was comparable to new soot in premixed flames (which also has been attributed to first-order acetylene reactions [3-9]).

In view of this status, a major issue is the nature of soot formation processes in diffusion flames involving hydrocarbon fuels other than acetylene. In particular, information is needed about the dominant gas species in the soot formation region and the impact of gas species other than acetylene on soot nucleation and growth. The study involved measurements of both flame and soot properties along the axis of laminar jet diffusion flames at pressures of 0.25-1.00 atm., considering ethane, ethylene, propane, propylene, butane and 1, 3-butadiene burning in air.

Experimental Methods. Two test arrangements were used to provide soot volume fractions on the order of 1 ppm for the various fuels: a low pressure burner having a 3 mm fuel port in a 300 mm diameter windowed chamber identical to the arrangement of Ref. [2], which was used to study heavily-sooting propylene and butadiene flames at 0.25 atm; and a coflowing laminar jet flame having a 10 mm diameter fuel port, similar to the arrangement used by Santoro and coworkers (cited in [2]), which was used for the remaining fuels at atmospheric pressure. The luminous portion of the test flames was 50 - 80 mm long.

Instrumentation used in the experiments was identical to Sunderland et al. [2]: soot volume fractions were found by deconvoluted laser extinction measurements, soot structure was found by thermophoretic sampling and analysis using TEM, gas velocities were found by laser velocimetry, gas temperatures were found by radiation corrected thermocouples (soot-free regions) and by deconvoluted multiline emission measurements (soot-containing regions), and gas species concentrations were found by sampling and gas chromatography.

Flame Structure. Typical soot and flame properties along the axis are illustrated in Fig. 1 for the propane/air flame at atmospheric pressure. Many features of the present flames are similar to the earlier results for acetylene/air flames [2]: significant levels of soot formation (based on increasing values of soot volume fractions) only are observed where temperatures exceed 1250K; significant soot formation ends when hydrocarbon concentrations become small, at a fuel-equivalence ratio of roughly 1.7; the soot formation region involves significant concentrations of O_2, CO_2 and H_2O, so that soot formation and oxidation proceed at the same time; and competition between soot nucleation and growth cause primary soot particles to reach their maximum diameter well before the end of the soot growth region. On the other hand, there are some interesting differences between the results for acetylene [2] and present results for other fuels: the soot formation region involves significant concentrations of ethylene and methane in addition to acetylene; and soot growth persists outside the acetylene-containing region so that soot growth reactions in addition to acetylene, must be present.

Soot Growth. Soot growth rates were found along the axis of the test flames similar to [2]. As before, soot growth rates exhibited small activation energies; therefore, they were correlated in terms of the concentrations of potential soot-forming hydrocarbon species. Initial results along these lines are illustrated in Fig. 2 for all the flames, where soot growth is plotted as a function of acetylene concentration. Results for the acetylene/air diffusion flames [2], as well as for premixed flames [3-8], also are shown on the plot. All these results represent gross soot growth rates, uncorrected either for effects of simultaneous soot oxidation or for growth by the direct reaction of hydrocarbons other than acetylene.

The results illustrated in Fig. 2 suggest comparable growth rates for acetylene/air diffusion flames and for new soot within premixed flames (the uppermost data points for premixed flames) as discussed in Ref. [2], with differences between these rates attributed to uncertainties of the reactive surface area for the premixed flames. In contrast, growth rates for the present hydrocarbon/air flames are significantly higher than the rest, suggesting the presence of soot growth channels other than the acetylene channel; this behavior is supported by the observation of significant rates of soot growth in regions where acetylene was absent.

In order to resolve effects of parallel soot growth channels, the raw growth data were corrected for effects of both growth by acetylene and oxidation by O_2, CO_2 and H_2O. The acetylene growth rate correction was based on [2], assuming an acetylene collision efficiency of 0.53%. Soot oxidation was evaluated similar to [2]: allowing for oxidation by O_2 using the rate expression of Nagle and Strickland-Constable [10], as later confirmed by Park and Appleton [11]; allowing for oxidation by CO_2 and H_2O following either Johnstone et al. [12] and Libby and Blake [13] or Bradley et al. [14]; while ignoring soot oxidation by OH, as discussed by Neoh et al. [15], because concentrations of OH should be small in the soot formation region due to the presence of hydrocarbon species [16, 17]. Proceeding in this manner it is possible to correlate the corrected growth rate with methane alone, however, present results will be limited to growth by ethylene alone because ethylene provides a more plausible soot growth mechanism.

The resulting correlation between soot growth and ethylene concentrations is illustrated in Fig. 3. Due to current uncertainties about soot oxidation estimates, results having oxidation corrections in excess of 60% of the growth rate have been excluded. The results do not exhibit any consistent trend with fuel type and temperature. Assuming first-order growth in ethylene concentration yields a very plausible collision efficiency of 1.8%; this correlation is illustrated on the plot. Nevertheless, the ethylene mechanism is only provisional at this stage because uncertainties of the order with respect to ethylene are rather large.

Soot Nucleation. The nucleation of primary soot particles was analyzed similar to Ref [2]. It was found that nucleation generally was associated with the presence of acetylene, and that the rates were similar to the earlier findings of [2] for acetylene/air diffusion flames. This implies a first-order reaction in acetylene with a modest activation energy. The resulting correlation is illustrated in Fig. 4:

good agreement between present results and those of Sunderland et al. [2] clearly is evident, yielding an activation energy of roughly 32 kcal/gmol. In addition, the results from this laboratory are roughly an order of magnitude smaller than earlier estimates by Leung et al. [18] which also are shown on the plot; this discrepancy is attributed to uncertainties in the optical methods used to estimate soot surface areas by Leung et al. [18].

Attributing soot nucleation to acetylene alone clearly is a massive simplification of a complex process involving large molecules, eventually growing to visible primary soot particles. Nevertheless, acetylene offers a plausible surrogate for these complex gas mixtures because the large molecular weight species can be expressed terms of acetylene through equilibrium constants, while acetylene is a major growth species as the large molecules evolve toward soot.

Nomenclature. [i] = molar concentration of i, d_p=mean primary soot particle diameter, f=mixture fraction, f_s=soot volume fraction, k_n=soot nucleation rate constant, n_p=number of primary soot particles per unit volume, T=temperature, u=streamwise velocity, v_g=soot growth velocity, w_g=soot growth rate, X_i=mole fraction of species i, z=streamwise distance.

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