

SOOT FORMATION AND BURNOUT IN FLAMES

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Foreseeable trends in fossil fuel availability indicate that the aromatic content of future fuels will be significantly higher than present levels. There are substantial economic and public health incentives to pursue the clean and efficient use of such highly aromatic fuels, especially as their strong sooting tendency is well known. For example, the Experimental Referee Broad Specification (ERBS) fuel, proposed by NASA as representative of a near-term alternate fuel for aircraft contains 29.6% of aromatics, as compared to 17.3% in Jet A aviation turbine kerosene.

The amount of soot formed when burning a benzene/hexane mixture in a turbulent combustor simulating gas turbine engines illustrates the expected effect of increasing the aromatic fraction (Fig. 1). Soot concentration profiles in the same combustor for kerosene fuel are shown on Fig. 2. Modeling these profiles requires the understanding of complex processes such as the chemistry of formation of soot precursors, the nucleation, growth and subsequent burnout of soot particles, and the effect of mixing intensity on the previous steps. The presentation will focus on recent results from experiments designed to shed light on these different processes.

While the strong sooting tendencies of aromatic hydrocarbons are well known, the underlying mechanism of this behavior is not established. Some experimental evidence suggests that the intact aromatic ring and not fragmentation products is responsible for the propensity of aromatic hydrocarbons to form soot. Accordingly, destruction of the ring during combustion might offer a route for the reduction of soot formation from aromatic fuels. To investigate these mechanisms, the structure of a near sooting, low pressure (20 torrs) benzene-oxygen-argon flame has been studied using a mass spectrometer coupled with a molecular beam sampling system¹. Some results in terms of mole fraction of molecular and radical species are shown in Figs. 3 to 6, and will be discussed in more details. They suggest that soot precursors are high molecular mass polyaromatic molecules. The process may start by addition of vinyl-acetylene to phenyl radical to form naphthalene (Table I). A benzyl-type radical is formed by methyl radical substitution at the α -position in naphthalene (Table II) and subsequent abstraction of a methyl hydrogen. The product of C_2H_2 addition to this benzyl-type radical can be rapidly stabilized by cyclization to form a six-membered ring through an internal aromatic substitution reaction. Such a mechanism will explain the strong sooting tendencies of methyl-substituted aromatics under a variety of conditions.

The nature of soot nuclei is not well established. A possibility is that the large polyaromatic molecules undergo coagulation, and once formed, the particles provide a surface on which gas phase material can deposit. Recent results² derived from laser-light scattering and absorption study of soot

formation in premixed and diffusion laminar flames reveal two regimes of soot particle growth. For soot volume fraction smaller than about 10^{-7} , the growing particles maintain an approximately spherical shape. At larger soot volume fraction, chain forming collisions occur, simultaneously with some surface growth. In both regimes, the particle number density is described by the free molecular collision theory, the final number of agglomerates being always close to $10^{10}/\text{cm}^3$ (Fig. 7).

In most practical combustors, soot burnout occurs at the end of the process, reducing the amount of soot released in the environment (Fig. 2). An ongoing program³ at M.I.T. is addressing the following questions 1) relative importance of the various oxidants O_2 , OH , O , CO_2 , and H_2O in soot oxidation, 2) effect of oxidation on the internal structure of the soot particles, 3) burnout characteristics of soot from premixed flames and from fuel pyrolysis, 4) effect of temperature-time history of soot formation on soot burnout. Results at this stage indicate that the specific burnout rates based on the external surface area of the particles are larger than predicted by the classical Nagle and Strickland-Constable formula. The N_2 BET surface area of soot increases considerably more during burnout than can be accounted for by the decrease of particle diameter, indicating opening of porosity. Under some conditions, a breakup of soot agglomerates appears to occur during the post-combustion.

Finally, in turbulent combustors⁴, the mixing characteristics of fuel and air can affect considerably the amount of soot produced and released in the atmosphere (Fig. 2 and 8). For some conditions (Fig. 8) the soot emission levels are in reverse order of maximum soot concentration, stressing the importance of burnout.

REFERENCES

1. Bittner, J.D.: Ph.D. Thesis, M.I.T. (in preparation)
2. Prado, G. et al: Submitted for Presentation at the 18th Symposium (International) on Combustion, Waterloo (Canada)
3. Neoh, K.: Ph.D. Thesis, M.I.T. (in preparation)
4. Prado, G. et al: 16th Symposium (International) on Combustion, p.649 (1977)

TABLE I: PHENYL RADICAL & VINYLACETYLENE

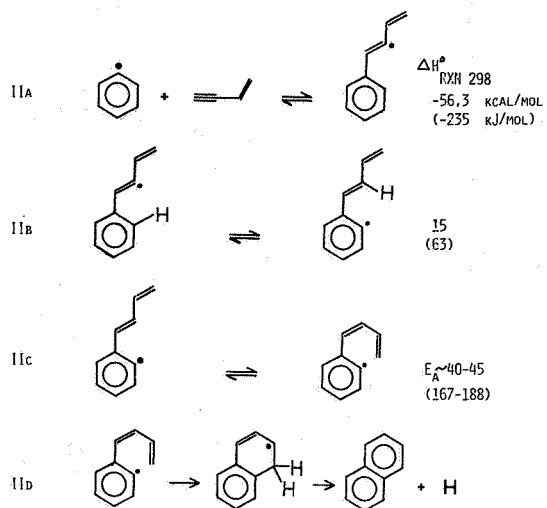
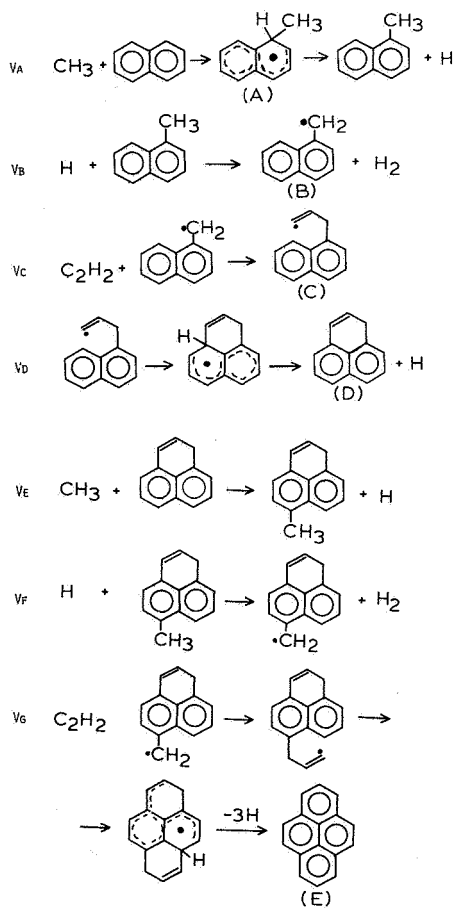


TABLE II: METHYL SUBSTITUTION



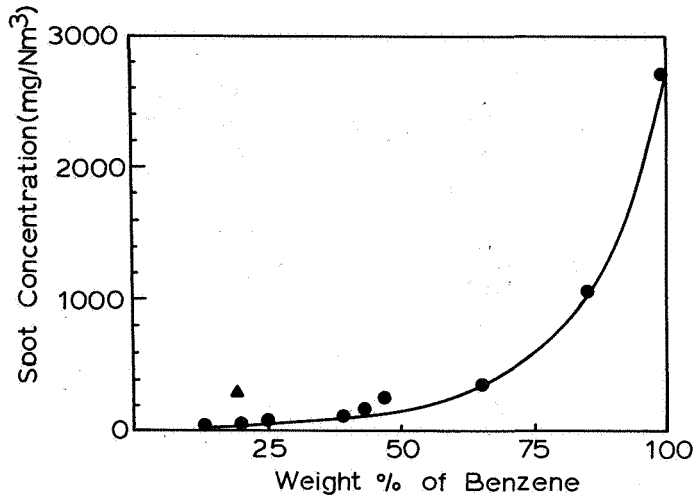


FIG. 1 INFLUENCE OF FUEL AROMATIC CONTENT ON SOOT CONCENTRATION TURBULENT COMBUSTOR. FUEL EQUIVALENCE RATIO = 1.0. ATOMIZING AIR PRESSURE = 184kPa. COLD GAS VELOCITY = 2.67 m/sec. (●) MIXTURE HEPTANE-BENZENE. (▲) KEROSENE

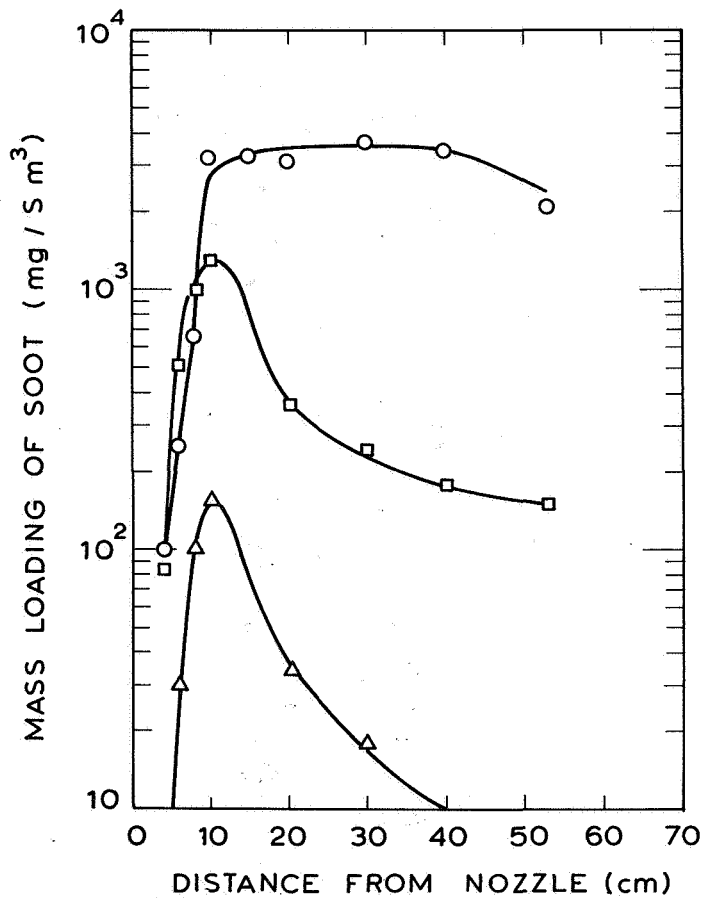


FIG. 2 INFLUENCE OF ATOMIZING-AIR PRESSURE ON AXIAL SOOT CONCENTRATION KEROSENE/AIR. FUEL EQUIVALENCE RATIO = 1.0. COLD GAS VELOCITY = 0.96m/sec. ATOMIZING-AIR PRESSURE = (○) 184kPa, (□) 205kPa, (▲) 239kPa.

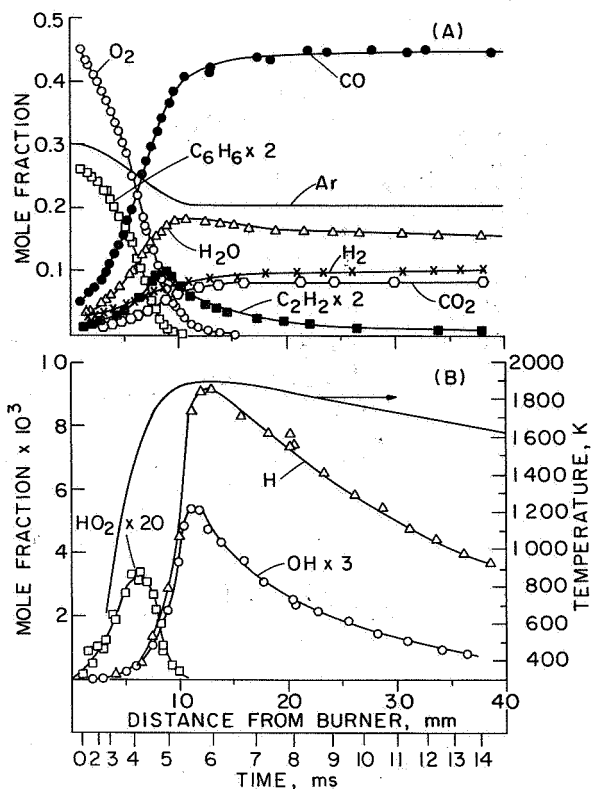


FIG. 3 MOLE FRACTION AND TEMPERATURE VS DISTANCE FROM BURNER IN A NEAR SOOTING ($\phi = 1.8$) BENZENE (13.5m%) OXYGEN (56.5m%) ARGON (30.0m%) FLAME. COLD GAS VELOCITY = 0.5m/sec. PRESSURE = 2.67kPa (20TORR). (A) MAJOR STABLE SPECIES. (B) H, OH, HO₂ AND TEMPERATURE

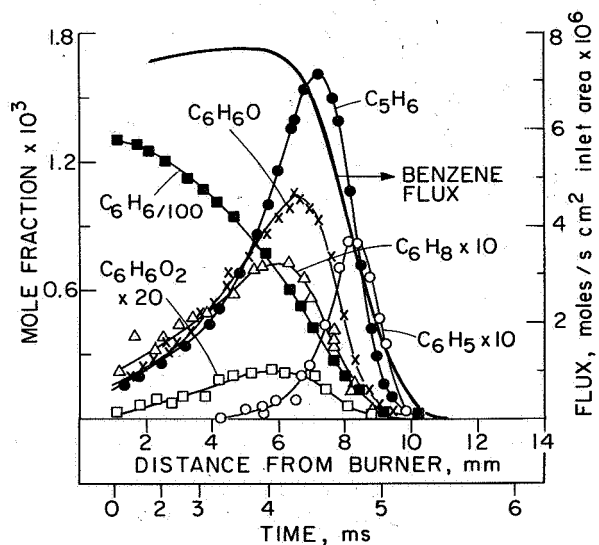


FIG. 4 FLUX AND MOLE FRACTION OF BENZENE AND MOLE FRACTIONS OF SPECIES OF POSSIBLE IMPORTANCE IN BENZENE DECOMPOSITION VS DISTANCE FROM BURNER IN A NEAR SOOTING ($\phi = 1.8$) BENZENE (13.5m%) OXYGEN (56.5m%) ARGON (30.0m%) FLAME. COLD GAS VELOCITY = 0.5m/sec. PRESSURE = 2.67kPa (20TORR)

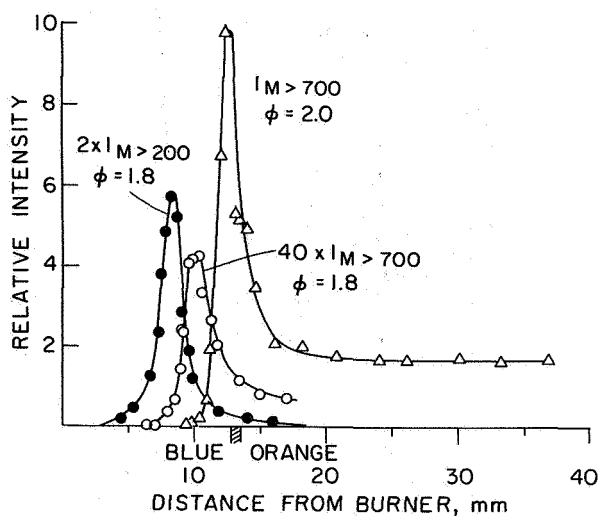


FIG. 5 RELATIVE INTENSITIES OF SIGNALS FROM HIGH MASS MODE OPERATION VS DISTANCE FROM BURNER. BENZENE-OXYGEN-ARGON FLAME. PRESSURE = 2.67kPa (20 TORR), COLD GAS VELOCITY = 0.5m/sec.

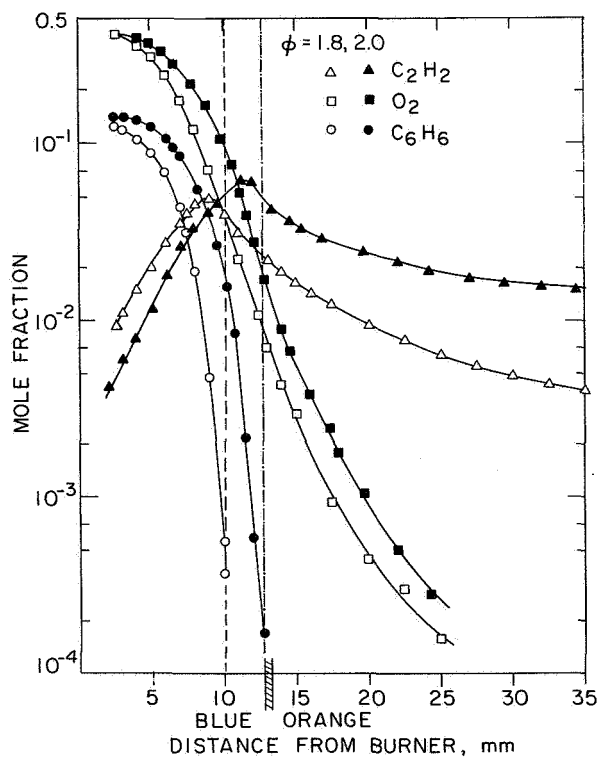


FIG. 6 MOLE FRACTION OF C_2H_2 , O_2 , and C_6H_6 VS DISTANCE FROM BURNER FOR NEAR SOOTING ($\phi = 1.8$, OPEN SYMBOLS) AND SOOTING ($\phi = 2.0$, SHADED SYMBOLS) FLAMES. BENZENE-OXYGEN-ARGON FLAME. PRESSURE = 2.67kPa (20 TORR). COLD GAS VELOCITY = 0.5m/sec.

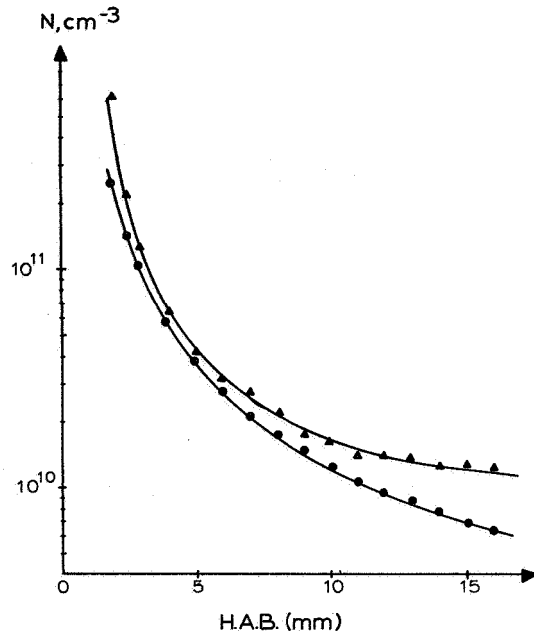


FIG. 7 EXPERIMENTAL (\blacktriangle) AND COMPUTED (\bullet) NUMBER DENSITY OF PARTICLES (N, cm^{-3}), PROPANE/OXYGEN FLAME. FUEL EQUIVALENCE RATIO = 2.5. ATMOSPHERIC PRESSURE. COLD GAS VELOCITY = 5.50cm/sec.

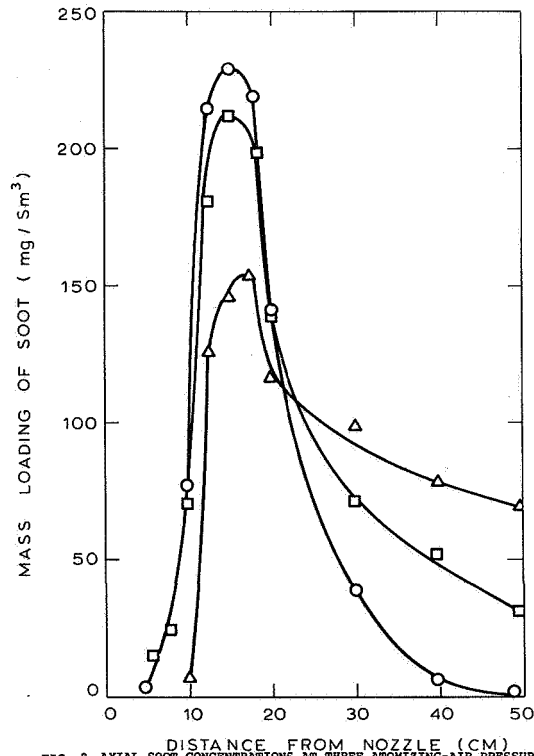


FIG. 8 AXIAL SOOT CONCENTRATIONS AT THREE ATOMIZING-AIR PRESSURE KEROSENE/AIR- FUEL EQUIVALENCE RATIO = 1.0. COLD GAS VELOCITY = 2.67m/sec. ATOMIZING-AIR PRESSURE = (O)184kPa, (□) 205kPa, (Δ)239kPa.