

CARBON NANOSTRUCTURE: ITS EVOLUTION DURING AND ITS IMPACT UPON SOOT GROWTH AND OXIDATION

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Introduction

Soot impacts the performance of power and propulsion systems, is a hazard of unwanted fires and is the main combustion generated pollutant. Responsible for an estimated 60,000 deaths per year in the U.S. alone, the EPA's new PM 2.5 criteria for particulate matter reflects increasing recognition of the health hazards associated with soot. Combustor ignitors and fuel injectors can become fouled with flame generated soot. Continuum radiation from soot is the main heat load upon combustor components and linings and is ultimately responsible for their failure. The spread of unwanted fires largely occurs through preheating from soot radiation. While an unwanted pollutant, soot also causes the release of substantial CO emissions from fires and unburned hydrocarbons in engines.

As most practical flames are turbulent diffusion flames, soot processes within such flames are of great relevance. Given the prevalent fuel-rich conditions at elevated temperatures within such flames, soot formation is inevitable. In contrast to seeking control of soot inception and growth, an alternative strategy is to focus on soot removal through oxidation. For example, modification of fuel/air mixing, reburning and exhaust gas recirculation represent parameters and processes that can be adjusted in existing practical devices to facilitate soot burnout by both O₂ and OH. Such process control and design require accurate models of soot oxidation processes. Current models for soot oxidation are inhibited by widely varying values for soot oxidation rates [1]. Values for OH collision efficiencies vary widely, ranging from 0.13 in premixed flames [2], to 0.3 in shock tubes [3] while from 0.11 to 0.01 in diffusion flames [4]. Similar uncertainties exist in O₂ oxidation rates with rates varying by factors of +6 to -20 relative to the Nagle Strickland-Constable rate for graphite oxidation [5].

An entirely neglected aspect in the relatively few oxidation studies performed to-date is soot nanostructure, its evolution during combustion and its impact on oxidation. Soot nanostructure is defined here as the local spatial arrangement and orientation of nanoscale graphene layers. In contrast, the relation between carbon structure and reactivity is well-known in carbon science from thermal and oxidative studies of coal, char and graphite [6-8]. Similarly for soot, as the nanostructure evolves, the relative number and accessibility of potential reactive carbon layer edge sites (aryl C-H bonds) changes. It is these sites that are potentially accessible for H-atom abstraction followed by molecular (acetylene) addition (HACA mechanism) [9], potential rearrangement and/or bonding with adjacent layer planes (graphene layer plane growth, i.e. graphitization) or for reaction with O₂ or OH (oxidation). Larger (longer) graphene layer planes, larger (and hence fewer) crystallites and concentrically oriented crystallites (lower edge site accessibility) result in fewer potential reaction sites for these reactions. In contrast, such structures are desirable towards purposeful synthesis of ordered carbon materials such as fullerenic structures [10].

To-date, there has been little systematic study of the soot nanostructure evolution during combustion as a function of thermal or oxidative treatments. Given this, it is not surprising that there is also an absence of detailed data regarding the impact of soot nanostructure upon oxidation processes (and rates) and upon purposeful growth of highly ordered carbon materials. Buoyancy-induced convection prevents logical independent variation of the temperature and residence time necessary for defining the range of conditions under which such changes occur. Consequently nanostructural changes in soot have yet to be directly studied within combustion processes and their impact quantified.

OBJECTIVES

In response to this void of knowledge and potential impact, it is main goal of the proposed research to demonstrate the importance of soot particle nanostructure by defining its degree of impact on oxidation and growth. Secondly, this research will examine the effect of chemical environment and temperature-time history upon the development of desirable ordered carbonaceous (fullerenic) nanostructures.

APPROACH

Microgravity will be used to provide a range of conditions for studying the influence of growth species, temperature conditions, their individual and combined effect upon the oxidation of the soot and synthesis of ordered carbon materials. Microgravity will allow the independent control of temperature and residence time for separating the solid state and gas-phase processes. In the absence of buoyancy, spatial gradients are relaxed to allow resolution of the soot nanostructure development. Temperature gradients are greatly reduced allowing intelligible temperature-time trajectories. Finally, residence times can be extended to investigate kinetic temperature dependencies.

In contrast to past experimental studies, these experiments will use direct measurements from transmission electron microscopy (TEM) images rather than inferences based only on light extinction and scattering for oxidation measurements and extraction-based procedures for fullerenic materials. High-resolution TEM (HRTEM) and image analysis will be used to quantify the soot graphitization and order levels in response to growth conditions, thermal and oxidative treatment, to assess the impact of nanostructure upon oxidation and to search for fullerenic structures through variation of inception/growth conditions. Soot surface nanostructure will be probed by scanning tunnelling microscopy (STEM). The soot collection will be performed by thermophoretic sampling. Flame measurements will consist of temperature via thermocouples and 2-wavelength pyrometry. The oxidizing species concentration and temperature will be measured directly using diode laser absorption spectroscopy. Combined with a characterized chemical environment, quantitative analysis of the impact of nanostructure upon soot oxidation and purposeful growth along specific trajectories in chemical environments at known temperatures will be enabled. Armed with experimental data, model development of soot oxidation including nanostructural changes can be developed and tested. The experimental configurations will consist of various dual flame configurations.

SUMMARY

The proposed work is a ground-based study to define and quantify soot nanostructural changes in response to growth conditions, thermal and oxidative treatments and to quantify their impact upon further oxidation and growth of highly ordered carbon materials. Experimental data relating soot oxidation rates to multiple oxidizing species concentrations will directly test for additive or synergistic soot oxidation rates. Such validation is central for assessing the applicability of individual soot oxidation rates and designing oxidative strategies for controlling soot loadings in and emissions from turbulent combustion processes. Through these experiments, new insights into soot nanostructure evolution during and its impact upon oxidation by O₂ and OH will be realized. It is expected that the results of this effort will spawn new research directions in future microgravity and 1g environments. Issues raised by positive or even negative demonstration of the hypotheses of this proposal have direct bearing on modelling and controlling soot formation and its destruction in nearly every combustion process producing soot.

ACKNOWLEDGEMENTS

This work is supported by a NASA NRA 99-HEDs-01 combustion award administered through NASA cooperative agreement NAC3-544 with The National Center for Microgravity Research on Fluids and Combustion (NCFM) at The NASA-Glenn Research Center.

REFERENCES

1. Kennedy, I. M., Prog. Energy Combust. Sci. 23:95 (1997).
2. Neoh, K. G., Howard, J. B. and Sarofim, A. F., in Particulate Carbon, D. C. Siegla and G. W. Smith (eds.) Plenum Press, New York p. 261 (1981).
3. Roth, P., Brandt, O. and Gersum, S. Von., Twenty-Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA p. 1485 (1990).
4. Haudiquert, M., Cessou, A., Stepowski, D. and Coppalle, A., Combust. and Flame 111:139 (1997).
5. Levendis, Y. A., Flagan, R. C. and Gavalas, G. R., Combust. and Flame 76:221 (1989).
6. Ljubisa, R., Walker, P. L. and Jenkins, R. G., Fuel 62:849 (1983).
7. Hurt, R. H., Dudek, D. R., Longwell, J. P. and Sarofim, A. F., Carbon, 26:433 (1988).
8. Rosner, D. E. and Allendorf, H. D., AIAA Journal 6:650 (1968).
9. Frenklach, M. and Wang, H., Twenty-Third Symposium (International) on Combustion, The Combustion Institute p. 1559 (1990).
10. Grieco, W. J., Howard, J. B., Rainey, L. C., Vander Sande, J. B., Carbon 38:597 (2000).-----

