NIRT: Understanding Robust Large Scale Manufacturing of Nanoparticles and Their Toxicology

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Overview:
While a myriad of options exist to manufacture so-called engineered nanoparticles, very few are industrially viable. Furthermore, no clear path exists to transition small-scale laboratory experiments to large-scale economically and environmentally viable processes. An additional concern is the unknown toxicological properties of engineered nanoparticles. To address the above issues, this project focuses on two thrust areas -- manufacturing process relationships and toxicological relationships – and involves an academic, government, industrial partnership, encompassing the disciplines of Chemistry, Chemical and Mechanical Engineering, and Medicine.

University of Maryland:
During the first year we have built, with partial support from the Cabot corp. a flame driven synthesis reactor. The reactor is designed to produce up to 100 g/hr of carbon and metal/carbon nanocomposite particles. The reactor is now operational and we have been generating particles. At the present time we are still dealing with some reactor instability issues. The reactor is now instrumented with an on-line scanning mobility particle sizing system so that real time size distribution measurements can be obtained. One of the motivations for this project was to generate new classes of carbon based nanostructures. To that end this year we have created what we call "Sea Urchin" like hybrid nanoparticle/nanotube structures [1]. These materials have been shown to enhance the thermal conductivity of fluids by as much as 20% for only a 0.2% volume loading of particle [2]. This year we have also developed a new approach to inject directly nanoparticles into solution thus preventing contamination/and agglomeration to corrupt the toxicological studies. The approach relies on condensing water vapor to each nanoparticle in free flight, thus growing each nanoparticle to a droplet of ~ 10um, so as to increase the momentum of the particle and enable efficient injection into solution.

Future work will involve completing the last few modifications to the reactor and begin to collect data on the role of fuel structure and catalyst loading on the yield, size, and structure of nanoparticles. Form these results we will down-select materials that will be

submitted to the Rochester Toxicology group. The data generated will also provide the basis for the work of the Yale group in modeling particle formation.

Yale University:
We have developed a model for nanoparticle formation that considers the soot kinetics as coalescing, solid carbon spheroids undergoing surface growth in the free molecule limit. The particle mass range of interest is divided into sections and an equation is written for each section including coalescence, surface growth, and oxidation. For the smallest section, an inception source term is included. The transport conservation equation for each section includes thermophoresis, an effective bin diffusion rate, and source terms for gas-phase scrubbing. The gas and soot equations are additionally coupled through non-adiabatic radiative loss in the optically-thin approximation. The inception model employed here is based on an estimate of the formation rate of two- and three-ringed aromatic species (naphthalene and phenanthrene), and is a function of local acetylene, benzene, phenyl and molecular hydrogen concentrations. Oxidation of soot is by O_2 and OH. The surface growth rate is based upon that of Harris and Weiner.

We have investigated the changing soot field as the dilution fuel fraction in the central tube changed. We were able to predict soot volume fractions along the wings of the flame in good agreement with experimental measurements; but we underpredicted soot volume fractions along the centerline [3,4]. This deficiency was particularly true for the flames with higher fuel mole fractions. To help understand the reasons for the transition of soot from the centerline to the wings of the flame as the fuel fraction increases, we began an investigation of the relative rates of inception, surface growth, and oxidation, along with a particle residence time analysis as a function of fuel fraction. While inception tends to peak on the centerline, the maximum in surface growth migrates from the centerline to the wings of the flame as the fuel fraction increases. Concurrently, the relative importance of surface growth and inception reverses. This change in the relative importance of these two subprocesses is due to the significant increase in residence time available for soot growth in the flame wings. Moreover, even with a significant increase in residence time along the centerline (and the local increase in fuel fraction) associated with the less diluted flames, the ageing of the soot particles and the lower temperatures inhibit the enhanced soot inception and growth along the centerline.

Future work will examine modifications to the kinetic mechanism to include metal addition. These reactions are being developed in collaboration with Dr. Wing Tsang of NIST.

University of Rochester School of Medicine:
During the last year we have been working to develop models that would prove useful in assessing the toxicity of carbon nanomaterials produced by this new process. The approach we have chosen is a multi-tiered set of analyses examining intrinsic properties of the material and interactions of nanomaterials with cellular systems leading eventually to assessment in appropriate animal models.

Our study of intrinsic properties has to date focused mainly on the ability of materials to generate reactive oxygen species in the absence of a biological substrate. This approach

is based on the hypothesis that many toxic responses arise to the induction of reactive species in cells and tissues. Our studies this year have established the measurement technique in our laboratory and we have screened an array of currently available carbon nanomaterials to establish a basis for comparison to those produced in the novel reactor. Our data suggest that although carbons do not generate high levels of reactive species, they are produced in a reproducible manner. Differences in reactivity seem to be most related to differences in surface area of the material and suggest this, and not mass may be a better metric.

Similarly, our studies in cellular systems have assessed measures of oxidative stress in cells likely to encounter particles after inhalation or as a consequence of translocation from lung into the systemic circulation. Measures of response include direct cell killing and the production of gene products induced by cellular oxidative stress. Our current results with benchmark particles show dramatic differences in induction of gene expression and, by inference, ability to induce cellular stress, but little direct toxicity. It is not clear whether these differences are due to trace contaminants on the particles or some other property. It does suggest that, as the particles from the current process become more available, we have a viable system to evaluate the potential for adverse effects. These studies form the basis of work in the coming year along with possible extension to animal studies (which will require considerably more material).

References:

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