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SIMULATION OF NUCLEATION, COAGULATION AND FINITE RATE SINTERING IN NANOPARTICULATE AEROSOL AGGREGATE FORMATION

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INTRODUCTION

An active interest has developed, of late, in the formation and growth of nanoparticles which emerge through aerosol mediated routes. Such particles play an important role in both natural and in engineered systems. In natural systems like the atmosphere, these particles may form from meteors (Bandyopadhyaya et al., 2004), sulfate and nitrate, although a host of other formation routes having important meteorological implications can be described (Friedlander, 2000). Soot aggregates from diesel exhaust are also causes of concern due to their deleterious effects on human health (Nemmar et al., 2004). On the other hand, high purity nanoparticles of silica, titania, iron, silver, nickel, carbon black etc. are produced in huge quantities in aerosol reactors worldwide. Used as pigments, catalysts and reinforcing fillers, the performance of these materials depends upon their size and morphology.

Through our work, we intend to simulate the formation of titania in a plug flow reactor, taking into consideration the phenomena of nucleation, coagulation and finite rate sintering. The Monte Carlo simulation scheme is a stochastic method, which has been used here for the discrete stochastic events, like nucleation and coagulation. By these processes, we intend to explore the product properties (number density of agglomerates, primary particle diameter, volume equivalent diameter and geometric mean diameter) as they evolve along the reactor length and compare with experiments.

METHODOLOGY

Initial State

An initial simulation volume V(0) is defined, which contains no particles.

Time Increment

Increment in time is performed using the principle of the interval of quiescence (Shah et al, 1977). It is the time interval in which no discrete event (nucleation or coagulation) takes place.

$$\tau = \frac{-\ln(1-u)}{f_t}$$

u = a uniformly distributed random variable

$f_t = f_n + f_c$

f_n = total nucleation frequency, same as reaction rate leading to titania formation; calculated using either Pratsinis et al (1990) or Moody and Collins (2003)

f_c = total collision frequency

Sintering

The increase in primary particle diameter due to sintering is calculated following Lehtinen et al (1996).

Event Selection

A relative frequency is defined as

$$y = \frac{f_n}{f_t}$$

The value of y is then compared with another value of u. If, $u \leq y$ nucleation is chosen as the next event, else coagulation is chosen. We use the method of inversion to select the specific coagulation pair (i,j) from among all possible pairs.

Time – Space Conversion

During the small increment in time τ, when an event occurs, the aerosol moves along the reactor from position x to x+Δx. The distance covered, Δx, is calculated as:

$$\Delta x = v(x)\,\tau$$

where v(x) is the axial flow velocity. The flow rate is updated using ideal gas-law, and the velocity calculated therein, on dividing by the cross sectional area.

Update of System Properties

The system properties updated are the simulation volume and number density. Simulation volume is updated using Charles' Law, and therefore expands or contracts with an increase or decrease in temperature, respectively. Also updated are the mean primary particle diameter (calculated following Lehtinen et al., 1996), volume equivalent and geometric mean diameters of the agglomerate population (Kataria, 2006, pp 75-76).

We use either of the two reaction rate expressions – one of Pratsinis et al. (1990) or that of Moody and Collins (2003), and see how the simulation predictions based on either of them compare with experimental data.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of four physical parameters: primary particle diameter, agglomerate number density, volume equivalent diameter, and geometric mean diameter, for three different temperatures, and for both the reaction rate expressions considered above. It is seen that at 1073 K, our simulation results using the rate expression of Moody and Collins (2003) predicts the experimental values very closely. At other temperatures, too, their rate expression gives a closer prediction of the experimental data for all the four physical parameters; as compared to that obtained from our simulation, on using the expression of Pratsinis et al. (1990). This could be explained by the fact that the rate expression of Moody and Collins (2003) gave a better fit to the experimental data of Pratsinis et al. (1990), as is seen in the former paper itself.

The thermophoretic deposition of titania on the reactor walls and in the sampling lines could be one of the reasons why the predicted values differ in some cases. with respect to the experiment. Another reason could be the assumption of plug flow in the tubular aerosol reactor, and a one dimensional temperature profile.

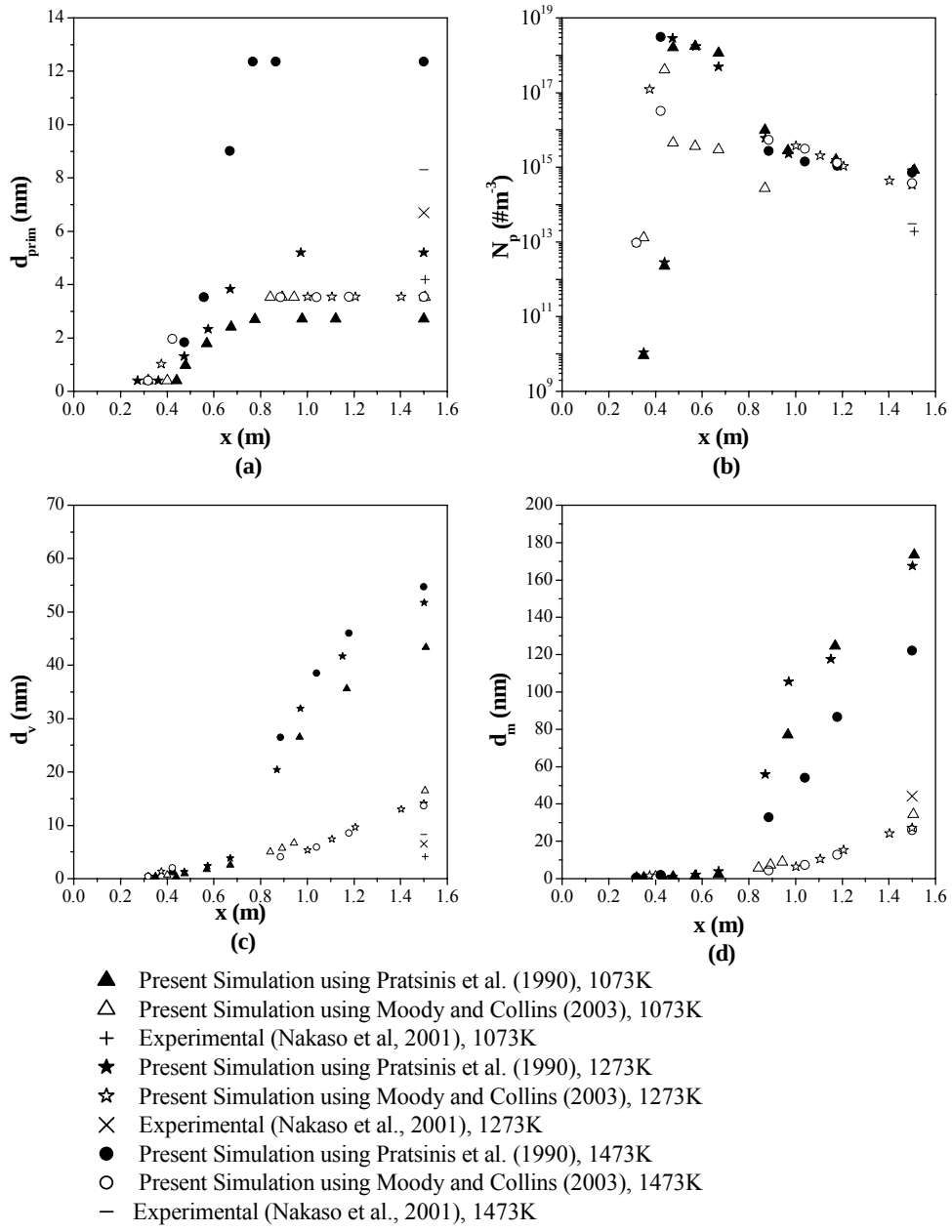

Fig. 1: Comparison of spatial evolution of (a) primary particle diameter (b) number density of agglomerates (c) volume equivalent diameter and (d) geometric mean diameter of titania nanoparticulate aggregates, as obtained from our Monte Carlo simulation (using two different rate expressions from literature) and experiments.

CONCLUSIONS

A Monte Carlo simulation scheme has been developed and tested for the formation of titania nanoparticles in a plug flow aerosol reactor. The evolution of three different size parameters, namely the primary particle diameter, volume equivalent diameter and geometric mean diameter have been tracked along the reactor length; the results compared with the experimental data of Nakaso et al. (2001). Our simulation results compare well with the experiments. The effects of two different rate expressions on our simulation results have also been assessed. It was found that the rate expression of Moody and Collins (2003), which was first order with respect to oxygen, gave a better fit to the experimental data as compared to that postulated by Pratsinis et al. (1990). The possible causes of deviation of the predicted values from the experimental data (on using either of the rate expressions) can be due to thermophoretic losses, assumption of plug flow and one dimensional temperature profile in the aerosol reactor.

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