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Numerical Simulation for Nanoparticle Growth in Flame Reactor and Control of Nanoparticles

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We review the models and numerical methods used in flame reactor for the modeling and simulation of nanoparticle. And we also review the control of nanoparticle size distribution, some nonlinear control strategies were looked into. A general model in which nanoparticles form in gas phase and grow through chemical reaction, nucleation, condensation and coagulation is discussed. Particles dispersed in a fluid move randomly, due to Brownian motion, and, along their trajectories, they collide with each other. The model is formulated in terms of a detailed population balance which describes how aerosol size distribution evolves with time. For this population balance models a number of different numerical approaches exist. We reviewed sectional, finite element and Monte Carlo methods, method of moments.

Keywords: Nanoparticles, Flame Reactor, Modelling, Population Balance, Numerical Methods.

REVIEW

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1. INTRODUCTION

In this article models of gas phase synthesis of nanoparticles in flame reactor and the numerical methods used to solve them were reviewed. The present topic can be used as a literature to review the whole history of combustion science and technology in the light of aspect of particle formation. Nearly every flame produces particles, which are sometimes quite visible and obvious in a sooting flame, but sometimes nearly invisible. Flames often appear to be particle free, because our eyes or the respective diagnostics are not sensitive or specific enough to detect them. We have learned to consider flames not only as a reactive flow with internal energy transfer, but also as a reactor for synthesizing mostly unwanted gaseous or particulate pollutants.

Development of nanomaterial involves several key steps. Firstly, synthesis of size and even shape of controlled nanoparticles is the key of developing nano devices. Secondly, characterization of nanoparticle is indispensable to understand the behaviour and properties of nanoparticles, aiming at implementing nanotechnology, controlling their behaviour and designing new material system with super performance. Thirdly, theoretical modelling is vitally important to understand and predicts material's performance. Gas phase combustion synthesis of inorganic particles is used routinely today to make a variety of commodities like, SiO_2, TiO_2, Al_2O_3, etc. amounting to millions of tons annually. They are used industrially as pigments, opacities, flowing aids for optical fibres and telecommunication. The flame reactor is the workhorse of this technology developed mostly in recent years. It has in some cases susperceded production routes by wet-phase chemistry.

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With the advancement in materials synthesis in recent years, it has been possible to embed nanoparticles with control size in bulk materials.[1] Although a number of gas-phase synthesis processes exist, they all have in common the essential aspects of particle formation processes that occur once the product species is generated. The product quality and application characteristics of nanostructured materials depend strongly on the size distribution, morphology and state of aggregation, i.e. the size and number of primary particles defining the degree of aggregation. In gas-phase reactors the final product qualities are determined by fluid mechanics and particle dynamics within a few milliseconds at the early stages of the synthesis process. Within this short timeframe, three major formation mechanisms dominate particle formation. The chemical reaction of the precursor leads to the formation of product monomers (clusters) by nucleation or direct inception and to the growth of particles via the reaction of precursor molecules on the surface of newly formed particles, which is called surface growth.

Coagulation is an essential process which occurrence at high particle concentrations is unavoidable in all industrial aerosol processes. Particles dispersed in a fluid move randomly, due to Brownian motion, and, along their trajectories, they collide with each other. Assuming strong adhesive forces, which are characteristic for small particles, these collisions result in coagulation. Finally, coalescence and fusion are sufficiently fast in the high temperature zones of the reactor to effect a reduction in the level of aggregation or even the formation of spherical particles, due to sintering processes.

Nanoparticles always have novel properties which can be used for the development of new improved processing, making the control synthesis of nanoparticles important to fields like chemistry, materials science and engineering, and the environmental sciences. Again, nanosized (i.e., smaller than tens of nanometres) particles often behave differently, both physically and chemically, then their larger counterparts. Thus, the synthesis of model materials for the fundamental mechanisms of nanoparticle transformations, nucleation and growth as well as the physical and chemical properties of nanoparticle are critical to understanding their behaviour in natural engineered systems. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is not often the case. Size-dependant properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and superparamagnetism in magnetic materials. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes very important. Particles with diameters in the range of 1∼100 nm are of great interest for fabrication of advanced high-performance. Typical ways of synthesizing the nanoparticles are wet chemical processing and aerosol processes. Aerosol processes have potential advantages for the production of nanoparticles with high yields and providing a molecular mixing for composite nanoparticles materials.[3]

Two very important aims which one hopes to achieve with knowledge gained through modeling are the

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improvement of yield and the quality of products and the scale-up of new processes from laboratory or bench scale level to an industrial level. In both cases the model needs to capture the essential physics and chemistry of the formation of nanoparticles, their interactions with each other and with the surrounding gas phase and their transport through surrounding media. This required detailed models of the chemical reactions and population of particles. Despite the recent progress in some of these areas, the predictive power of the current models remains poor. The ability to model the shape and size of a population of nanoparticles is extremely vital as these properties may affect the physical attributes of the final product. The use of population balance models to study nanoparticle growth has become widespread, especially when studying nanoparticle forms in flames.[4–5]

In the research community it has been recognized that it is important to study system which are simpler than a spray injected into a reactor of complex geometry. For this reason a number of laboratory experiments have been developed, the simplest being a shock tube; other experiment configuration include plug flow reactors, jet stirred reactors, premixed flames and counter flow. Whereas for industrial applications only simplified models are available there exist detailed models for laboratory scale experiments. The findings obtained from these experiments and attempts to model them are summarized in review articles and number of text books which are the best sources of further information of nanoparticles and their applications. Selections of these sources are discussed below.

The book by Friedlander[6] is a classic text book and is more relevant to nanoparticles as it consists detail population balance modelling especially on agglomerate formation and reconstructing. A more general text on population balances is a book by Christofides[7] which describes some numerical techniques for the population balance models to control an aerosol flow reactor. Important articles in the area of soot include the article by Kennedy[8] which contains collections of references and also described a detailed soot model. In addition, the book on Nanoscience, engineering and technology edited by William et al.[9] is recommended. It contains a collection of chapters which addresses the important issues concerning the engineering challenges and modeling electron in nanoscale, nanoparticle manipulation by electronic forces, contributions of molecular modeling to nanometre-scale science e.t.c.

The aim of this paper is to provide the up to date review of the literature which is concerned with modelling of nanoparticle of population dynamics and also the control of particle size distribution. A variety of numerical approaches were discussed. The paper is structured as follows: discussion of flame reactor, outline of the general population model, computer simulation and the numerical approaches are reviewed; control of particle size distribution is also reviewed. Finally, new areas of future research are identified.

2. FLAME REACTOR/FLAME SYNTHESIS

Gas-phase reactions are characterised by very high temperatures and extremely short residence times. The manufacturing process and conditions determine the size and morphology of the product and hence their suitability in given fields of application. Flame reactors are one of the most common reactor designs for the production of high-purity nanostructured materials in large quantities, especially for the production of silica, titania and alumina. Powders, liquids and vapours can be used as precursors. Due to the high energy density in the flame, the precursor concentration can also be quite high, with flame temperatures reaching 1,000–2,400 °C. The residence time in the highest temperature region is very short, usually between 10 and 100 ms. This hot zone is crucial for the formation of the primary particles, which in this process range from only a few nm up to 500 nm. Beyond this zone, only the size and the morphology of the aggregates can be influenced. The shape of the flame can be influenced by the type of fuel and air inlet used. If the gases are premixed, the flame reaction takes place right at the burner mouth, creating a very short, homogeneous flame. With diffusion flames, the fuel and the air or oxygen is fed separately to the burner mouth. The reactants have to diffuse together before they can combust, which creates a significantly longer flame.

Flame synthesis is a cost-effective and versatile industrial process for inexpensive materials; it also offers advantages over alternative material synthesis processes. The high temperature flame reactor can be designed for wide range of operating conditions. The process is self-purifying with respect to the final powder product. The characteristics of flame-made particles are controlled by the following: the time–temperature behaviour, including rapid quenching of the gas/particle flow, the mixing of the reactants and precursor and the overall composition. The required particle should be high purity with a well controlled size distribution and morphology, which depends on particular application. Besides the large scale industrial flame synthesis reactors, combustion scientist have studied particle synthesis nearly all type of flames, including burner—stabilized premixed flat flames, stagnation point premixed flames, coflow flames, counter flow flames, and multidiffusion flames. Also well-stirred reactors and non-stationary flames in closed vessels have been used to synthesis particles. The early research were focused on the development of new technologies and had to demonstrate control over the process. The control and characterization of the particulate product with respect to size, structure, and morphology was quite limited. Also new devices for characterising material properties (X-RAY, TEM, SEM, and others) have contributed to the understanding finetuning of particle synthesis.[10] The control of particle characteristics during flame synthesis is crucial because the properties of materials of materials made from

these particles depend on size and size distribution, morphology, extent of aggregation and chemical and phase composition.[11]

2.1. Principle of Particle Formation and Growth from Gas Phase

Nanoparticles are mostly synthesized in laboratory flames by adding a precursor dopant in gaseous of liquid state, to the unburnt gas. Such precursors are often compounds of metals like halides or organometals. They are sometimes dissolved in water or in liquid hydrocarbons. The kinetics of the combustion reactions are only loosely coupled to the precursor's decomposition and the reactions forming particles. The energy of the exothermic oxidation reaction is used to increase the temperature of the fluid flow, thus driving the chemical reaction s of the precursor gas. This results in vaporization of droplets of a liquid precursor, thereby initiating its decomposition. Nuclei and clusters are formed, which further grow to nanoparticles by surface grow to nanoparticles by surface growth and/or coagulation and coalescence. This is similar to what is known about soot formation in flames.

This type of synthesis of particles in a fluid flow can also be established by using energy source other than combustion to start or sustain the partly endothermic reactions of the precursor. Particularly advantageous for the synthesis of non-oxide or metallic particles are hot wall reactors, plasma reactor, or laser reactors. They are all simple devices in which energy for increasing temperature is transferred from a hot wall or is directly coupled in the form of micro wave or laser energy into the fluid flow. They are quite useful and can extend the synthesis of flame-made oxide particles to the huge class of oxygen-free particles.

2.2. Particle Inception

Particle inception is the transition from gas phase compounds to nascent molecular particles. It is probably the most difficult part when modeling nanoparticle synthesis. It is fair to say that it is not really understood.[12] It is also the least understood step in the formation of particle at high temperature. Characterisation of the nascent particles and of their transformation in different flame conditions is crucial to understand the full mechanism of particulate formation. The fact is that number, size and chemical properties of the nascent particles strongly affect the amount and size distribution of particles emitted from combustion processes. The current picture of particle formation in combustion suggests that very small particles with sizes down to 1–2 nm are formed, but their nature and role in soot particle formation is still object of research.[13] In particular, the composition as a function of the flame temperature, or fuel composition deserve a deeper study since nascent nanoparticles might be soot precursors but they also may constitute part of the particulate matter emitted at the exhaust of combustion source.

One approach to model particle inception is using detailed kinetic mechanism to model the flame structure and particle formation.[13] This mechanism provides both gas phase reactions and particle sections. The mechanism includes reactions for the pyrolysis and oxidation of the fuels and growth of small radicals leading to the formation of high-molecular compounds. Steven et al.[14] studied the sequence of formation events in high temperature regime, i.e, particle structured and dynamic. Here growth of inception particles of PAH was simulated using the atomistic model particle inception AMPI which is design to couple the Kinetic Monte Carlo and molecular dynamic techniques to bridge the time scale between and during reaction events. The AMPI code was used in their work to produce an ensemble of nanoparticles at a specific location in an ethylene premixed flame. The intermolecular scale between the nanoparticles is described using a coarse-grained molecular dynamic approach. A large particle ensemble has been effective to observe a statistical significant number of coagulation events. This corresponds to running force field-based molecular dynamic of over millions of atoms for simulation times on the order of hundreds of nanoparticles, which cannot be achieved in a reasonable research time frame. One option is to depart from an all atom calculation, and in essence lower the resolution. A multiscale coarse-grained method in which detailed atomistic models transformed into lower resolution model via a systematic and thermodynamically consistent procedure in which pre-selected atomic group were collected into new coarse-grained quasi-units was used. The most crucial and challenging stage in the implementation of the above approaches is the determination of the intermolecular forces to describe the interactions between the new effective coarse grain sites.

2.3. Surface Reaction

To model surface reaction accurately, it is important to understand the gas-phase chemistry, chemical composition and the surface area of nanoparticles. Surface area plays an important role in many applications. Together with particle sintering, surface area can significantly change the fractal dimension of particle.

3. OUTLINE OF GENERAL MODEL

3.1. Modeling Aspect

The formation of nanoparticles in a flame can be formally described by combining the laws for a flowing and reacting fluid with the population balance equation for suspended particles. If the precursor is sufficiently dilute, the flow field can be decoupled from the particles' rate processes and delivers the temperature and transport field for the

formation and growth of particles. For axisymmetric laminar flames of cylindrical geometry, a further simplification can be made by reducing the spatial variables to one axial coordinate z. Initially, the modelling effort to describe a particle's evolution from molecular dimensions to nanosized particles necessarily focuses on idealizations. Most time, only coagulation of particles was considered with the assumption of instantaneous coalescence. Only one particle state variable, i.e., the volume v of a particle, was taken into account. The problems associated with the evolution of particle size can be illustrated by discussing the population balance equation below. In the case of particle coalescence, the interdependence of sintering and agglomeration must be fully taken into account. Agglomerates with partly fused primary particles must be expected.

3.2. Computer Simulation

The control of reactor parameters, such as temperature profile, residence time in the hot zone and concentration of the reaction partners, is of great importance in producing tailor-made nanostructured materials. However, linking process parameters measurably to product characteristics requires an excellent understanding of the physicochemical fundamentals of gas phase synthesis.

Although the basic process was developed several decades ago and extensive empirical know-how has been accumulated, the formation mechanisms are not yet fully understood. Measurements in gas-phase reactors are quite problematic, as time scales are very small, temperatures are extremely high and the gaseous atmosphere is often aggressive. Therefore, computer simulation can be employed in fundamental investigations and may provide a better roadmap for product and process optimisation. Processes with particulate matter increasing and decreasing in amount and size over time can be described mathematically by so-called particle population balance models (PPBs).

3.3. Population Balance Model

We first lay out a general model for the population dynamics of nanoparticles. The population balance equation consists of the following nonlinear partial integro-differential equation.[15]

$$\frac{\partial n}{\partial t}+\frac{\partial(G(v,z,\bar{x})n)}{\partial v}+c_z\frac{\partial n}{\partial z}-I(v^*)\delta(v-v^*) = \frac{1}{2}\int_o^v \beta(\tilde{v},v-\tilde{v},\bar{x})n(\tilde{v},z,t)n(v-\tilde{v},z,t)\,d\tilde{v} - n(v,z,t)\int_o^\infty \beta(v,\tilde{v})n(\tilde{v},z,t)\,d\tilde{v} \quad (1)$$

In this model, The first term on the left hand side of Eq. (2) describe the change in the number concentration of particle volume interval v, $v+dv$ and in the spatial interval z. $z+dz$, $n(v,z,t)$ denotes the particle size distribution function, v is particle volume, t is time, $z\in[0,L]$ is the spatial coordinate, L is the length of the process. The second term on the left hand side gives the loss or gain of particles by condensational growth, the third term on the left hand side which is $c_z(\partial n/\partial z)$ corresponds to the convective transport of aerosol particles at fluid velocity c_z and the fourth term on the left hand side accounts for the formation of new particles of critical volume v^* by nucleation rate I. $I(v^*)\delta(v-v^*)$, also accounts for gain and loss of particles by condensation. $G(v,z,\bar{x})$, $I(v^*)$ and $\beta(\tilde{v},v-\tilde{v},\tilde{x})$ are the nonlinear scalar functions and δ is the standard Dirac function. The gain and loss of particles by Brownian coagulation is described by the first and second term on the right hand side of Eq. (1) respectively.

$$\frac{1}{2}\int_o^v \beta(\tilde{v},v-\tilde{v},\bar{x})n(\tilde{v},z,t)n(v-\tilde{v},z,t)\,d\tilde{v} - n(v,z,t)\int_o^\infty \beta(v,\tilde{v})n(\tilde{v},z,t)\,d\tilde{v} \quad (2)$$

$G(v,z,\bar{x})$ and β are the condensational growth and collision frequency function respectively. The nucleation rate $I(v^*)$ is assumed to follow the classical Becker-Doring theory given by the expression below (Pratisinis).[16]

$$I = n_s^2 s_1 (k_B T/2\pi m_1)^{1/2} S^2 (2/9\pi)^{1/3} \cdot\Sigma^{1/2}\exp(-k^* InS/2), \quad (3)$$

where s_1 is the monomer surface area and k^* is the number of monomer in critical nucleus and is given by:

$$k^* = \frac{\pi}{6}\left(\frac{4\Sigma}{InS}\right)^3, \quad \text{Where } \Sigma = \gamma v_1^{2/3}/k_B T \text{ and } \gamma \text{ is the surface tension.} \quad (4)$$

4. NUMERICAL METHODS

The numerical solution of Eq. (1) is a very challenging problem for so many reasons. The most important ones are:

(1) The large size of the system of partial integro-differential equation systems (where the independent variables are time, space and one or more internal particle coordinates, such as particle volume and shape). For example in the case of the coalescent sphere model, the different between the smallest and largest particle sizes and therefore the sizes of Eq. (1) can easily be several orders of magnitude.

(2) The nonlinearity of the coagulation operator: Nonlinearity usually arises from complex reaction, nucleation, condensation and coagulation rates and their nonlinear dependence on temperature. The complex nature of nanoparticle process models has motivated an extensive research activity on the development of numerical methods

for the accurate computation of their solution. Numerical models can be viewed as mathematical frameworks that permit the interaction of complex physical processes to be simulated. The first step in developing a numerical aerosol model is to assemble expressions for the relevant physical processes, such as chemical reactions, nucleation, condensation, coagulation, etc. The next step is to approximate the particle size distribution with a mathematical size distribution function.

Surface reactions and particle inception can also cause severe numerical challenges. In this section we shall discuss different strategies to obtain meaningful numerical solutions to Eq. (1) despite these difficulties. The following are examples of solution methods.

4.1. Sectional Methods

Sectional methods (SM) are widely used to solve population equations. In these methods, the size spectrum is divided into a set of size classes. In so doing, distinguishes between zero-order and higher-order methods. Higher-order methods use low order polynomials to represent the particles within each section and can be regarded as a simple form of finite elements methods and will be discussed in the next section. They can suffer from stability problems and artificial dispersion; whereas zero-order methods are more robust. Using sectional methods, computational domain is divided into rather small intervals in which the solution is approximated by step functions. For each interval, one obtained an ordinary differential equation which is coupled to neighbours depending on the discretization scheme used. Debra and Sonia[17] described a single moment sectional model to simulate the evolution of an aerosol distribution that contains more than one chemical component. The proposed method is based on dividing the particle domain into X sections with time variant sections boundaries.

To alleviate the problem with numerical diffusion in the presence of the surface growth,[18–20] introduced a pivot technique combined with a moving grid and also the method of characteristics. An additional method set of equation is solved to ensure that a chosen set of properties is conserved.[21] coupled a sectional model to a detailed gas phase mechanism to calculate the soot particle size distribution in a continuous stirred tank reactor (CSTR).

An alternative to bivariate population balances with volume and surface area as internal coordinates is to average the surface area information for each volume section, thereby turning a bivariate population balance into two univariate population balances. Different strategies are used to do this. Ashish and Panagiotis[15] used the sectional model to divide the continuous particle size distribution (PSD) into a finite number of sections within which the size distribution function is assumed to be constant. Suddha and Mark[22] used the sectional method of moment to approximate the continuous size distribution by a finite number of sections or bins within which one numerically conserved aerosol property is held constant. Jae and Mansoo,[23] developed two sets of sectional equations that describe the evolution of particle volume and surface area. The equations are based on; (1) sectional formulation for evolution of particle volume concentration and (2) sectional formulation for the evolution particle area concentration.

4.2. Finite Element Methods

Another method apart from the sectional methods is the more sophisticated finite element methods. In the finite element approach, the solution of the population balance is expanded in series of polynomials. For the coefficients of this expansion, a set of equations has to be solved and this is obtained by inserting the expansion into the population balance equation. Various methods can be derived by different nodes, functions, and time stepping schemes. The mathematical discipline of functional analysis provides the theoretical framework with which errors can be estimated. This is of course a very attractive feature of finite element methods.

James and Panagiotis,[24] proposed a finite-dimensional approximation and control of nonlinear parabolic partial differential equation (PDE) systems by combining Galerkin's method with the concept of approximate initial manifolds, known as non-linear Galerkin's method. Aleck and Costas[25] used orthogonal collection of finite element methods to solve a continuous form of general population balance equation (PBE). Hailian et al.[26] developed a predictive controller for parabolic convection–diffusion–reaction systems operating in convection-dominated regimes, using the combination of finite differences approximation of the diffusion term and the method of characteristics. Dan et al,[27] designed a control algorithm on the basis of finite dimensional models to capture the dominant dynamics of particulate processes.

4.3. Monte Carlo Methods

An alternative to sectional methods for solving the population balance equation are Monte Carlo (MC) methods. They are easy to implement, can account for fluctuations, and can easily incorporate several internal coordinates. In the case of nanoparticle modelling, the number of particles is so large that the fluctuations in particle numbers can be neglected.

One of the applications of Monte Carlo methods is the stochastic Monte Carlo (MC) method which is based on the principle that the dynamic evolution of an extremely large population of particles, $Np(t)$, can be followed by tracking down the relevant particle events (i.e., growth, aggregation, nucleation). Meimaroglou et al.[28] used this method.

The kinetic Monte Carlo (KMC) method is used to estimate and control methodologies for surface properties (e.g., surface roughness). Dan et al.,[27] developed Kinetic Monte-Carlo simulators of a surface based on small lattice size models to capture the dominant roughness evolution and utilize the available surface roughness measurements to improve upon the predictions of the kinetic Monte-Carlo simulators in order to obtain accurate surface roughness estimates.

Direct Simulation Monte Carlo (DSMC) method is also used to simulate aerosol particles. The Direct Simulation Monte Carlo algorithm works as follows. First, a normalization volume is chosen; then the solution to the population balance is approximated by N particles. The normalization volume plays the role of a numerical approximation parameter. Over the last decade the DSMC has been improved by several research groups in the engineering community. Most of these improvements can be classified as variance reduction techniques.

Monte Carlo methods can be easily extended to multiple internal coordinates and for this reason they have been employed to simulate various systems of nanoparticles. Akhtar et al.[29] included two internal coordinates to describe the restructuring of the particles and showed the time evolution of mass fractal dimension. Monte Carlo methods have also been used to model coating of nanoparticles and to simulate the growth of single aggregates and study the effect of surface growth or sintering on the fractal dimension and other properties of the aggregate.

4.4. The Least Square Method

The least squares method (LSM) is a well-established technique for solving a wide range of mathematical problems. The basic idea in the LSM is to minimize the integral of the square of the residual over the computational domain, in the case when the exact solutions are sufficiently smooth the convergence rate is exponential. Daora and Jakobosen,[30] applied the least square method to solve the population balance equation.

4.5. Methods of Moment

The method of moments (MOM) is computationally the most efficient approach to obtain a numerical approximation to the moments of population balance. For this reason, this method is often used when simulating problems where transport of particles in a flow with complex geometry is essential. In the area of nanoparticle modelling, two techniques have been used so far. One of the techniques is the quadrature method of moments (QMOM) which is a more recent technique. Dorao and Jakobson[31] derived (QMOM) in two ways, i.e., the standard quadrature method of moments which is a numerical closure for method of moments (MOM) and the method of moments in the method of weighted residuals (MOM-MWR).

The second technique is the method of moment with internal closure (MOMIC). Diemer and Ehrman[32] developed a design for the comparison of reconstructed distributions from moment with direct calculation via sectional method. The design was used to probe sensitivity of distribution reconstruction and problem solution to model size for both the MOMIC and QMOM approaches. Barret and Webb[33] compared some approximation methods for solving the aerosol dynamic equation. The methods compared are quadrature method of moments, the finite element method (FEM), Luguerre quadrature and Associated Laguerre quadrature. Suddah and Mark[22] also used quadrature method of moments to solve the problem of obtaining closure of the moment equations, for the coagulation, growth, diffusion and thermophoretic terms to be expressed in their original forms.

In the first instance MOMIC has been developed to describe the formation and oxidation of soot particles. In its early form, the method is based on univariate description of spherical soot particles in the free molecular regime. An alternative approach for obtaining the moments of the PSD is the quadrature method of moments (QMOM). In this method, the moments are calculated assuming the PSD can be represented as weighted multi-dimensional Dirac delta function. The weights and the nodes are then chosen to satisfy the transport equations for the moments of the PSD. The advantage of this approach is that due to the choice of delta functions, there exists no closure problem. Gerber and Mousavi[34] applied the quadrature method of moments to the polydispersed droplet spectrum in transonic steam flows with primary and secondary nucleation.

Despite all the computational advantages there are some shortcomings associated with the methods of moments. The most significant shortcoming is the non-uniqueness of the reconstruction of the particle size distribution function (PSDF). As a consequence, reactions that take place on the particles' surface which lead to decomposition of particles back to the gas phase can only be incorporated with additional model assumptions.

5. CONTROL OF PARTICLE SIZE DISTRIBUTION

Aerosol processes are increasingly being used for the large scale production of nano-and micro-sized particles. The processes have largely replaced other processes which involve multiple steps of wet chemistry, due to the direct gas phase chemical reaction of precursor vapour and the ease of separation of the particulate products from the gas. Ashish and Panagiotis[15] developed a nonlinear feedback control method for spatially-inhomogeneous aerosol processes for which the manipulated inputs, the control objectives and the measurement were distributed in space. Their starting point was the general nonlinear partial integro-differential equation describing processes

with simultaneous chemical reaction, nucleation, condensation, coagulation and convective transport. Then under the assumption of lognormal aerosol size distribution, the method of moments was employed to reduce the original model into a set of first-order hyperbolic partial differentia equations (PDEs) which accurately described the spatio-temporal evolution of the three leading moments needed to exactly characterize the aerosol size distribution. This hyperbolic PDE system was then used as the basis for the synthesis for nonlinear distributed output feedback controllers that use process measurement to achieve aerosol size distribution with desired characteristics (geometric average particle volume). Ashish and Panagiotis[35] applied their control method to an aerosol flow reactor to produce titania powder by gas phase oxidation of titanium tetrachloride. The controller manipulates the temperature of the reactor wall to achieve an aerosol size distribution in the outlet of the reactor with desired geometric average particle diameter. The performance and robustness of the nonlinear controller was successfully tested through computer simulations and found to outperform linear control techniques. Ashish and Panagiotis[36] derived and solved sectional representations and unimodal lognormal moment approximations of population balance model. From their research it was found that the moment model provides reasonable accurate estimates of the average properties of the aerosol size distribution computed by sectional model for long times. Then a nonlinear estimator is constructed on the basis of the moment model, which employs measurements of the geometric average particle designed on the basis of the moment and is implemented on the sectional model to achieve an aerosol size distribution with desired geometric average particle diameter.

6. FUTURE DEVELOPMENT

Despite the progress in the last few years at modeling of nanoparticle flame synthesis there is clearly a need for further development of models and numerical methods. Homogeneous and heterogeneous chemical reactions need to be understood to model particle formation and the change in particle size due to chemical reactions on the particle surface. Currently the data on thermodynamic properties of relevant species and chemical reaction mechanisms are either missing or have high uncertainties associated with them. It is important to conduct more high quality experiments in order to determine the relevant data. However, the role of computational chemistry will become more important as computers become more powerful so that thermodynamic properties and chemical reaction kinetics can be obtained.

Another area which needs to develop further is the development of mathematical techniques for estimating parameters in population balance models from experimental data. A weighted Monte Carlo method for the calculation of parametric derivates has been developed.[37] This method has a large potential to determine physical parameters from experimental data in area of nanoparticles. Scientifically, only the modeling of homogeneous gas phase nanoparticle synthesis has been studied. It is important to know that in many applications the precursors of the particles are sprayed into flame. There they form particles under the appropriate conditions.[38] This means that the dynamics of the droplets including the precipitation within the droplets needs to be included in the population balance model. Model developed in the area of spray drying are suitable stating point to achieve this.

An area which is very important in the modelling of nanoparticles is the development and the control strategies in order to control the particle size distribution. Few models for this process have been looked into in this paper but it is an important field in the future. Not until recently, the rich literature on population balance modelling, numerical solution, and dynamical analysis of particulate processes, research on model-based control of particulate processes had been very limited. Specifically, early research efforts had mainly focused on the understanding of the fundamental control-theory properties. The interest in control of particulate processes has been triggered by the need to achieve tight control of particle size and its distributions that greatly influence particulate product properties and quality. Drawing from recent advances in dynamics of infinite-dimensional systems and nonlinear control theory, control of particulate processes using population balances has evolved into a very active research area within the field of process control. In spite of the rich literature on population balance modelling, numerical solution, and dynamical analysis of particulate processes, research on model-based control has been limited[39] and there is need to control this particulate processes in order to achieve tight control of particle size and its distributions.

7. CONCLUSION

Particle synthesis in flames is an overlapping field of research; it can be explored from two directions: material science and combustion science. It may be erroneously considered to be at the fringes of both disciplines, but it can contribute to and benefit from both. Material science is interested in solid state products, including nanomaterials with tailored new properties. In this paper we reviewed the literature of nanoparticles from flame synthesis and discussed models and numerical methods used in this field. We also reviewed the control of particle size distribution. We started describing a general population balance model for nanoparticles. This model is comprised of several processes which are: gain and loss of particles by condensational growth, convective transport of aerosol particles, nucleation rate which is the formation of new particles and gain and loss of particle by Brownian coagulation. The numerical treatments of population balances

were reviewed. The literature on the sectional method, finite element method, Mont Carlo method and method of moments were discussed. Understanding the dynamics of larger, highly structured aggregates, which appear later in a flame, is not driven much by processes like chemical reactions. It is therefore obvious that the very early processes in a flame, like precursor decomposition, monomer formation, cluster kinetics, and the early formation of particles should be the natural playground of combustion researchers. As all the processes addressed are strongly controlled by temperature, this property must be carefully measured, together with the concentrations of species in the region of particle inception. This seems to be even more important for those particles with mixed components, where the chemistry becomes critical.

The control of particle size distribution was also examined, it is an important area that brings together fundamental modeling, numerical simulation, nonlinear dynamic and control theory. The method of moment was found to be more efficient and suitable for the control of particles size distribution. Finally, future areas of research were developed. The integration of population balance modelling and advanced control into the chemical engineering course of research will be essential for chemical engineers to play important role in expanding this field.

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