PRIMARY AND AGGLOMERATE AEROSOL DYNAMICS

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LIST OF CONTENTS

LIST OF CONTENTS | 1
ZUSAMMENFASSUNG | V
SUMMARY | VII
INTRODUCTION | IX

1. A REVIEW ON MODELING OF SOOT FORMATION AND GROWTH 1
ABSTRACT | 1
1.1. INTRODUCTION | 1
1.2. BACKGROUND | 2
1.2.1. Soot, Fullerenes and Carbon Black | 2
1.2.2. Formation and Growth Aspects | 3
1.2.3. Measurement Techniques | 4
1.2.4. Effect of Electric Fields | 5
1.3. SOOT MODELS | 5
1.3.1. Classification of Models | 5
1.3.2. Summary of Previous Basic Models | 6
1.3.3. Recent Advances in Soot Modeling | 12
1.4. AEROSOL DYNAMICS MODELING | 21
1.4.1. Numerical Methods | 21
1.4.2. Coagulation with or without Gas Phase Chemical Reaction | 23
1.4.3. Coagulation of Non-Spherical Particles (Coagulation and Sintering) | 27
1.4.4. Coagulation (of Spherical Particles) and Surface Growth | 29
1.5. CONCLUSIONS | 31
1.6. REFERENCES | 32

2. SINTERING TIME FOR SILICA PARTICLE GROWTH | 42
ABSTRACT | 42
2.1. INTRODUCTION | 42
2.2. THEORY | 45
2.2.1. Aerosol Dynamics Model | 45
2.2.2. New Characteristic Sintering Time 47
2.3. RESULTS AND DISCUSSION 50
2.4. CONCLUSIONS 60
2.5. NOTATION 60
2.6. REFERENCES 62

3. POPULATION BALANCE MODELING OF FLAME SYNTHESIS OF TITANIA NANOPARTICLES 66
ABSTRACT 66
3.1. INTRODUCTION 66
3.2. EXPERIMENTAL 70
3.3. THEORY 74
  3.3.1. Reaction Models 74
  3.3.2. Moving Sectional Aerosol Dynamics Model 76
3.4. RESULTS AND DISCUSSION 82
  3.4.1. Validation 82
  3.4.2. Flame Temperature and Precursor Conversion 85
  3.4.3. Integral Aerosol Dynamics and Comparison with Experimental Data 86
  3.4.4. Evolution of Primary Particle Size Distribution 92
3.5. CONCLUSIONS 99
3.6. NOTATION LIST 100
3.7. REFERENCES 102

4. POPULATION BALANCE MODELING OF SYNTHESIS OF TITANIA NANOPARTICLES IN ELECTRICALLY ASSISTED PREMIXED FLAMES 108
ABSTRACT 108
4.1. INTRODUCTION 108
4.2. EXPERIMENTAL 112
4.3. THEORY 113
  4.3.1. Reaction Model 113
  4.3.2. Charging Model 113
  4.3.3. Moving Sectional Aerosol Dynamics Model 115
4.3.4. Monodisperse Aerosol Dynamics Model 118
4.3.5. Post Processing of Results 119

4.4. RESULTS AND DISCUSSION 120
4.4.1. Validation 120
4.4.2. Temperature Profiles 126
4.4.3. Particle Growth (primary particle size distributions) 128
4.4.4. Particle Growth (integral properties) 133

4.5. CONCLUSIONS 143
4.6. NOTATION LIST 143
4.7. REFERENCES 146

5. OUTLOOK FOR FUTURE IMPROVEMENTS IN AEROSOL DYNAMICS MODELING 152
5.1. REFERENCES 155

APPENDIX A 156
A.1. Modification of the aerosol dynamics model for gas phase chemical reaction 156

APPENDIX B 157
B.1. Applicability of chemical reactions 157
B.2. References 158

APPENDIX C 159
C.1. Derivation of the effect of surface growth on aggregate area concentration 159
C.2. References 160

APPENDIX D 161
D.1. Extension of the fixed sectional model of Hounslow et al. (1988) for coagulation and sintering 161
D.2. References 162
ZUSAMMENFASSUNG


Das Verwenden von elektrischen Feldern während der Flammensynthese von Keramik-Partikeln ist eine vielversprechende Technik, um sowohl die Partikelgrösse und Polydispersität als auch die Aggregatsstruktur und Kristallinität präzise zu kontrollieren. Die Bedeutung von elektrisch geladenen Partikeln während der Flammensynthese von Titandioxid-Nanopartikeln durch TTIP Zerlegung wird in
Kapitel 4 untersucht. Dabei wird das monodisperse und das bewegte sektionale Modell erweitert, um sowohl Feld- und Diffusionsaufladung, elektrostatische Koagulation als auch Partikeldispersität und Migrationsverluste zu berücksichtigen. Vergleiche zwischen im Institut gewonnenen experimentellen Daten und Modellvorschlägen über die durchschnittlichen primären Partikeldurchmesserverteilungen entlang der Flammenachse werden für eine Vielzahl von verschiedenen Gasvolumenströmen am Einlass durchgeführt.

SUMMARY

The present thesis is related to the understanding of the dynamics of interactions of nanosized particles suspended in gases (aerosols). More specifically, the main objective is to develop models accounting for the key parameters directly affecting the evolution of both aggregate and primary particle size distributions during the formation and growth of nanoparticles, such as titania (TiO$_2$) and silica (SiO$_2$), in aerosol flame reactors. Many aspects (experimental as well as computational) in aerosol dynamics have emerged from research relevant to soot formation in combustion processes. A review of the current modeling advances in that area is therefore presented in Chapter 1 where generic numerical schemes regarding basic particle growth mechanisms such as coagulation, sintering and surface growth are also explicitly discussed. A major consideration in these models is accuracy versus computational power demand and formulation complexity.

For many researchers, nanoparticles constitute a new state of matter as a large fraction of their molecules lies on the surface. Their properties are therefore different than those of the corresponding bulk material. Within this context, a novel sintering time for silica (SiO$_2$) nanoparticles is here developed (Chapter 2) accounting for the effect of nanosize structure in contrast to classical sintering models solely based on bulk material properties. The proposed characteristic sintering time is tested using a monodisperse model for aggregate dynamics by coagulation and sintering. Numerical predictions are in fairly good agreement with experimental data for silica formation and growth by oxidation of hexamethyl-disiloxane (HMDSO) and silicon-tetrachloride (SiCl$_4$) in premixed flames.

Another challenging aspect is the numerical modeling of particle dynamics involving a series of concurrent pathways such as gas phase chemical reactions, surface growth, coagulation and sintering (Chapter 3), typically encountered during synthesis of nanoparticles in aerosol flame reactors. The population balance equation describing the above mechanisms is an integro-differential equation (known as Smoluchowski’s equation) lacking (in the general case) analytical solution. Among several numerical techniques proposed to tackle the problem are sectional and monodisperse models. The former models consider the whole particle size distribution, while the latter neglect particle size polydispersity. Here efficient monodisperse and moving sectional quantitative tools (validated by comparisons with detailed but cumbersome literature models at certain limiting cases) are developed to explore the significance of various particle formation routes during flame synthesis of titania nanoparticles by titanium tetraisopropoxide (TTIP) decomposition in a premixed methane-oxygen flame by comparing detailed measured and calculated size distributions.

Application of electric fields during flame synthesis of ceramic particles is a promising technique that allows for precise control of the powder size and polydispersity as well as aggregate structure and crystallinity. In Chapter 4, the significance of particle charging during the electrically-assisted flame synthesis of titania nanoparticles by TTIP decomposition is investigated by extending the monodisperse and moving sectional models of the previous chapter to account for field and diffusion charging, electrostatic coagulation as well as particle dispersion and migration losses. Comparisons between in-house experimental data and model predictions monitoring average primary particle diameters and primary particle size distributions along the flame are carried out for a variety of inlet gas flowrates.
An outlook discussing the direction of future investigations and improvements pertinent to the current thesis is given in the last chapter. Detailed molecular dynamics simulations on silica clusters and additional comparisons of sectional calculations with experimental data for a wide variety of process conditions should be carried out for a complete investigation of the effects and applicability of the proposed silica particle sintering time. Likewise, more accurate predictions of primary particle size distributions could be achieved (in the expense of computational power, though) by expanding the proposed sectional model described in Chapter 3 from one to two dimensions (covering both particle volume and surface area coordinates). Finally, the description of particle formation and growth in complicated flow patterns (typically encountered in aerosol diffusion flames as well as in the presence of strong external electric fields) can be achieved by implementing in-house particle dynamics software in conjunction with efficient (commercial) codes for computational fluid mechanics.
INTRODUCTION

The main objective of this thesis is to develop models accounting for the key parameters affecting the evolution of both agglomerate and primary particle size distributions during the formation and growth of nanoparticles in aerosol flame reactors. These parameters mainly involve simultaneous coagulation and sintering of polydisperse particle populations, typically encountered during synthesis of a variety of aerosol-made powders such as soot, titania (TiO$_2$) and silica (SiO$_2$).

Many aspects (experimental as well as computational) in aerosol dynamics have emerged from research relevant to soot formation in combustion processes, as soot (in its general form, including several grades of carbon black) is the oldest and largest, by production volume, aerosol-made commercial product. Almost all stages of aerosol particle dynamics (such as nucleation, surface reactions and agglomeration) are encountered during soot formation and growth. A review of the current modeling advances in that area is therefore presented in Chapter 1. Typically, in this field more focus has been given on chemistry and turbulence mixing than on detailed aerosol dynamics. Hence, numerical schemes regarding basic particle growth mechanisms such as coagulation, sintering and surface growth (that can be applicable to most of the aerosol-made particles) are also explicitly discussed. A major consideration in these models is accuracy versus computational power demand and formulation complexity.

For many researchers, nanoparticles constitute a new state of matter as a large fraction of their molecules lies on the surface. Their properties are therefore different than those of the corresponding bulk material. Within this context, a novel sintering time for silica (SiO$_2$) nanoparticles is developed in Chapter 2 accounting for the effect of nanosize structure in contrast to classical sintering models solely based on bulk material properties. Silica is selected as it is the standard agglomerated material and is commercially marketed as such. The proposed characteristic sintering time is tested using a monodisperse model for aggregate dynamics by coagulation and sintering, while numerical predictions are compared with data from in-house experiments (carried out by Mr. Heiko Briesen at the University of Cincinnati) as well as data from the open literature for silica formation and growth by oxidation of hexamethyl-disiloxane (HMDSO) and silicon-tetrachloride (SiCl$_4$) in premixed methane-oxygen flames.

Another challenging aspect is the numerical modeling of agglomerate and primary particle dynamics involving a series of concurrent pathways such as gas phase
chemical reactions, surface growth, coagulation and sintering (Chapter 3). The population balance equation describing the above mechanisms is an integro-differential equation (known as Smoluchowski's equation) lacking (in the general case) analytical solution. Among several numerical techniques proposed to tackle the problem are sectional and monodisperse models. The former models consider the whole particle size distribution while the latter account for a single average particle size. Here, efficient monodisperse and moving sectional quantitative tools accounting for simultaneous gas phase chemical reaction, coagulation, sintering and surface growth are developed for the first time to explore the significance of various particle formation routes during flame synthesis of titania nanoparticles by titanium tetraisopropoxide (TTIP) decomposition in a premixed methane-oxygen flame. The above system is selected here, as titania is one of the most common large-scale, aerosol-made, ceramic commodities. In addition, formulations for titania nanoparticle sintering rates and TTIP surface reactions are readily available in the open literature.

Application of electric fields during flame synthesis of ceramic nanoparticles is a promising technique that allows for precise control of the agglomerate and primary particle size and crystallinity. In Chapter 4, the significance of particle charging during the electrically-assisted flame synthesis of titania nanoparticles by TTIP decomposition is investigated by extending the monodisperse and moving sectional models of the previous chapter to account for field and diffusion charging, electrostatic coagulation as well as particle dispersion and migration losses. Comparisons between in-house experimental data and model predictions monitoring average primary particle diameters and primary particle size distributions along the flame are carried out for a variety of inlet gas flowrates. It should be noted that all in-house experimental measurements in Chapters 3 and 4 (with the exception of the statistical analysis of pictures from transmission electron microscopy), have been carried out by Mr. Hendrik K. Kammler.

Finally, an outlook on the direction of future investigations and improvements pertinent to the current thesis is given in the last chapter (Chapter 5) discussing possible useful contributions from detailed molecular dynamics and computational fluid mechanics calculations.
1. A REVIEW ON MODELING OF SOOT FORMATION AND GROWTH

ABSTRACT

Soot is one of the most well known products of combustion. Yet, there is still a great deal of uncertainty regarding the detailed chemistry and physics of its formation, growth and oxidation. Here, the latest modeling advances are investigated mainly focusing on results from the last four to five years, following the major review of Ian M. Kennedy on the same issue in 1997. Generic numerical models of particle (aerosol) dynamics accounting for basic growth mechanisms such as coagulation, sintering and surface growth are also explicitly discussed.

1.1. INTRODUCTION

Soot is a common product in a wide variety of combustion systems such as premixed and diffusion flames, internal combustion engines, and gas turbines to name a few. The main sequence of chemical and physical phenomena relevant to its formation and growth have been in the fabric of intensive scientific research for many years. Basic research on this field has not been driven merely by pure scientific motivation but also by increasing requirements for more efficient performance of combustion engines and stringent air pollution control regulations. Although this effort has already led to significant advances, there are still aspects of the detailed chemistry of soot inception, surface reaction and oxidation that are not fully understood.

The main objective of the present review is to explore the most recent breakthroughs in modeling soot formation and growth, namely (with few exceptions) from the last four to five years following the major review of Ian M. Kennedy on the same issue in 1997. Background information will be first provided regarding fundamental aspects such as differences between soot and carbon black, soot structure, properties and chemistry as well as critical inception species, surface growth and oxidation. Several characteristic soot models (covering both gas phase chemical reactions and particle-particle interactions) with an emphasis on current results (after 1997) will be later discussed. Finally, particle dynamics numerical models (for instance, monodisperse, sectional, discrete sectional and moment methods) accounting for
various combinations of coagulation, sintering and surface growth will be explicitly investigated. Nevertheless, it should be pointed out here that the most remarkable differences between modeling efforts stem from the degree of analysis of the complex chemical kinetics.

1.2. BACKGROUND

1.2.1. Soot, Fullerenes and Carbon Black

Soot is typically a major by-product of high temperature pyrolysis or combustion of organic compounds usually detected in domestic fireplace chimneys, diesel engines, oil and coal furnace chambers or even urban dust. From a medical point of view it is an important species as it absorbs various polyaromatic hydrocarbons (PAHs) some of which with carcinogenic effects (Koshland, 1996). In general, soot particle mass ranges from roughly 2000 u to $10^8$ u (Homann, 1998) consisting mostly of carbon, as well as of inorganic compounds, organic tars and resins. However, there is no specific chemical formula designating soot as its composition strongly depends on the given process conditions and the fuel used (Heidermann et al., 1999; Colbeck et al., 1997). In contrast to fullerenes, common soot particles have filled interiors and less orderly structures containing several per cent of heteroatoms (Homann, 1998). Some similarities though, on important structural, electrical and magnetic features between certain grades of fullerenes and soot seem to exist (Dunne et al., 1997).

By the same token, common nomenclature for carbon black and soot should be avoided as there are many differences in origin, function, composition, purity or even morphology. More specifically, carbon black is an industrial product (widely used as a filler, modifying the mechanical or electrical properties of plastics and rubber) manufactured under controlled conditions (namely, flame pyrolysis and partial combustion of a hydrocarbon feedstock (Lahaye and Prado, 1978; Haynes and Wagner, 1981)) and characterized by a well-defined structure, consisting almost entirely of aciniform carbon with very small amounts of tars and other extraneous materials (for instance the soluble organic fraction, removable by toluene, is less than 0.3 %, while the fraction of ash is less than 1 %) (Medalia and Rivin, 1982). Nevertheless, there are also cases where certain grades of carbon black have properties similar to those of soot (Bonnefoy et al., 1994). Finally it should be noted that basic steps of soot formation and growth could also be applicable to carbon black (Lockwood and Van Niekerk, 1995).
1.2.2. Formation and Growth Aspects

Many experiments have been carried out in shock tubes, laminar premixed and diffusion flames leading to a great deal of information with respect to the prevailing mechanisms of soot formation and growth. The abundance of experimental data and process conditions studied has also caused contradictory conclusions concerning the necessity of detailed kinetic rates spanning nearly through all phases of soot production, from initiation reactions to surface oxidation (Kennedy, 1997). However, such controversies could be resolved, after elucidating the key role of soot mass fraction. Indeed, for lightly sooting flames Colket and Hall (1994) found an almost direct proportionality between soot inception rate and soot total mass fraction. At increasingly sooting flames though, this dependency rapidly decreased and was eventually replaced by surface growth processes (Hall et al., 1996). Similar conclusions were drawn later on by Pratsinis and Spicer (1998) when studying gas phase synthesis of titania from TiCl$_4$.

Hence, in the most general case, a full-blown predictive model for soot, typically includes, an inception step followed by particle coagulation, surface growth and surface oxidation reactions. Soot production is initiated by the formation of the first stable PAHs (Frenklach et al., 1984). The smallest detectable soot particles have sizes in the order of 1 nm (Kennedy, 1997). Although PAHs are essentially planar (two-dimensional) molecules, three-dimensional soot particles emerge from several layer fragments of PAHs oriented in a rather parallel fashion with respect to the surface (Homann, 1998). The appropriate neighboring of five and six-membered rings could also play a role in the structural evolution of soot particles, since when five-membered rings are adjacent to more than two six-membered rings, strong molecular distortions occur leading to the formation of bowl-shaped structures (Homann, 1998). It should be noted here that there are also proponents of the idea that the initial soot nucleus is an ion (Calcote et al., 1994). The fact is that the discussion on the validity of this argument has not finished yet (Hall-Roberts et al., 2000), while the acceptance of the ionic viewpoint is still limited (Kennedy, 1997).

Soot growth proceeds by coagulation and surface reactions in conjunction with the competitive effects of surface oxidation by molecular oxygen, OH radicals and other species such as O atoms, H$_2$O and CO$_2$ (Kennedy, 1997). Particle surface area concentration and active sites (Wieschnowsky et al., 1988) are apparently two crucial parameters associated with soot surface growth. Acetylene (C$_2$H$_2$) is considered as the
dominant surface growth species while PAHs may also play a role (Howard, 1990). Recently, Kazakov and Frenklach (1998a) presented a numerical test, which demonstrated that the use of acetylene as growth species did not actually contradict the experimental results of Benish et al. (1997). More specifically, they stated that Benish et al. (1997) had reached the opposite conclusion (namely, that PAHs were the major growth species) from an inappropriate assumption in their data reduction technique (they assumed equal C$_2$H$_2$-PAHs and C$_2$H$_2$-soot collision efficiencies, $\gamma$, while $\gamma[C_2H_2\text{-PAHs}]$ should have been much smaller than $\gamma[C_2H_2\text{-soot}]$).

1.2.3. Measurement Techniques

Many of the results discussed above require an elegant combination of experimental evidence and model predictions. Moreover, experiments should be appropriately designed to cover all the crucial phases of particle formation and growth. Especially, the early stage of particle formation is one of the areas that is ripe for better understanding as instruments that allow non-intrusive measurements are becoming available. Fourier transform infrared (FTIR) spectroscopy is for instance particularly attractive as it concurrently provides information on the flame temperature, gas composition and particle concentration (Best et al., 1991; Morrison Jr. et al., 1997; Farquharson et al., 1998). Thermophoretic sampling (TS) is also becoming widely used for particle collection from different locations along a flame and subsequent analysis with transmission electron microscopy (TEM) (Dobbins and Megaridis, 1987). Other relevant experimental analysis techniques include dark field TEM (DF-TEM) for detecting different crystallographic layer planes within soot particles (Vander Wal, 1998), high resolution TEM (HRTEM) and selected area electron diffraction (SAD) for detecting the degree of carbonization (Vander Wal, 1997), color video imaging for observations of the luminous flame shapes, deconvoluted laser extinction imaging for measuring soot volume fractions, deconvoluted multiline emission imaging for measuring soot temperature distribution (Urban et al., 1998), light scattering for quantitative analysis of particle/aggregate parameters such as mass fractal dimension, primary particle diameter and primary particle number per aggregate (Köylü, 1996; Ivezic et al., 1997), small angle x-ray scattering (SAXS) for estimation of the static structure factor of soot fractal aggregates (Sorensen et al., 1998), laser induced fluorescence (LIF) for estimation of OH and soot concentration profiles in high
temperature flames (Haudiquert et al., 1997) and even laser induced incandescence (LII) for in-situ measurement of soot primary particle size under certain conditions (Vanderwal et al., 1999).

1.2.4. Effect of Electric Fields

Finally, it should be interesting to mention the efforts of various research groups who try to control soot emissions in flames by applying electric fields. More specifically, Saito et al. (1999) used brass-plate / brass-ring electrodes and found that positive voltages corresponding to field intensities of over 200 kV/m could increase flame temperature by up to 500 °C and suppress soot emissions by more than 90 % in an acetylene diffusion flame (in agreement with earlier results by Saito et al. (1997) who used a simpler nozzle- electrode configuration). It was concluded that ionic winds enhanced mixing between the fuel and surrounding gas, thus inducing high flame temperatures which promoted soot reduction by oxidation. Similarly, Ohisa et al. (1999) showed that a single DC corona discharge or a discharge from three AC coronas (with the electrode tips outside the reaction zone) could reduce soot emissions without noticeable change in the luminous part of a turbulent propane / hydrogen diffusion flame. In this case it was concluded that inorganic charged species and electrons, entrained into the flame either by corona winds and diffusion (for DC coronas) or mainly by diffusion (for AC coronas), reduced the population of ion precursors relevant to soot emission.

1.3. SOOT MODELS

1.3.1. Classification of Models

Generally, there are three major categories in soot modeling: Purely empirical, semi-empirical (reduced or simplified) and detailed models. Purely empirical models are very popular in studies relevant to gas turbines and diesel engines. They provide general guideline-correlations (for instance, for soot volume fraction or concentration) and include a number of constants (adjustable parameters) appropriately tuned to achieve good agreement with baseline experimental data. Therefore, results from empirical modeling attempts should be treated with caution when extended to process conditions significantly different from those originally considered. Semi-empirical models are on the next level of complexity as they additionally incorporate physical and
chemical aspects of combustion in terms of simplified soot kinetics and particle dynamics. Again, it should be stressed that the degree of empiricism intrinsically included in these models restricts their fidelity within the proximity of the initial conditions of their calibration. On the other hand, detailed models can break through the ring fence of the above limitations by combining full-blown soot kinetics with particle growth mechanisms. However, even in this case, there may be certain limitations as the implementation of intricate chemical reaction schemes can lead to many modeling uncertainties in the calculations. A thorough and critical review of the above mentioned categories of soot modeling was recently carried out by Kennedy (1997). The recent modeling efforts discussed later on (after a brief description of previous basic models), are presented in a chronological order. Nevertheless, a similar classification to the one chosen by Kennedy (1997) is also shown in Table 1-1.

### 1.3.2. Summary of Previous Basic Models

Before summarizing current results (mainly after 1996), it would be useful to quickly revise some of the most crucial and widely applied detailed-soot models which can be used as basic starting points for further development. Frenklach et al. (1984) presented a detailed kinetic model for soot formation in shock-tube pyrolysis of acetylene which became the main core of future attempts too (Mauss et al., 1994; Nemeth and Heberger, 1998; Appel et al., 2000, to name a few). The reaction (consisting of approximately 600 elementary reversible reactions of 180 species) described acetylene pyrolysis, formation of larger molecules and radicals as well as formation and further (planar) growth of aromatic rings. Reaction rate coefficients were either calculated from laboratory measurements or taken to be reasonable collision theory upper limits. Soot species were chosen to begin from coronene (C\textsubscript{24}H\textsubscript{12}) while the pericyclic growth process was extended to infinity by means of a lumping procedure.

The prevailing formation pathway of the first aromatic ring from an aliphatic fuel, such as acetylene, was vinyl addition. Growth of aromatics continued through reactivation to radicals by hydrogen abstraction, and subsequent acetylene addition (H-abstraction/C\textsubscript{2}H\textsubscript{2}-addition: HACA). Sensitivity analysis of equilibrium constants revealed that the main rate limiting step (bottleneck) appeared at the formation of the first aromatic ring. The proposed reaction scheme was in accord with experimental data.
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Reaction Scheme</th>
<th>Fuel</th>
<th>Variables Solved</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soot Models Involving No Chemistry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hayashi et al. (1999)</td>
<td>Cluster-cluster aggregation only</td>
<td>Benzene</td>
<td>Aggregate shape, peripheral fractal dimension and size distribution</td>
<td>Fuel (1 mol %) pyrolysis in a hot wall furnace reactor</td>
</tr>
<tr>
<td><strong>Empirical Models</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kellerer et al. (2000)</td>
<td>Overall correlation for the soot volume fraction</td>
<td>Methane, ethylene, acetylene, propane, n-heptane, Benzene, Toluene</td>
<td>Soot volume fractions and particle number densities at different pressures and temperatures</td>
<td>Fuel rich oxidation and pyrolysis in shock tubes at high pressures (10-60 bars)</td>
</tr>
<tr>
<td><strong>Semi-Empirical (Reduced or Simplified) Models</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chao et al. (1998)</td>
<td>Simplified three-step reaction scheme</td>
<td>Ethylene</td>
<td>Flame sheet location, flame temperature, and other grouped variables relevant to several flame characteristics</td>
<td>Nonpremixed counter-flow flames</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Reaction Scheme</td>
<td>Fuel</td>
<td>Variables Solved</td>
<td>Application</td>
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<td><strong>Semi-Empirical (Reduced or Simplified) Models</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhang and Ezekoye (1998)</td>
<td>Reduced 8-step gas phase chemistry along with a reduced 4-step scheme for soot kinetics (Fairweather et al., 1992)</td>
<td>Methane</td>
<td>Contour plots for velocity, temperature, intermediate species concentrations, as well as soot volume fraction, surface growth, particle number density and oxidation rate</td>
<td>2-dimensional, confined coflow fuel/air jet diffusion flames</td>
</tr>
<tr>
<td>Kronenburg et al. (2000)</td>
<td>Soot inception and surface growth as first order functions of acetylene concentration</td>
<td>Methane</td>
<td>Temperature, soot particle number density, mixture fraction and soot volume or mass fraction profiles</td>
<td>Turbulent fuel/air jet diffusion flames</td>
</tr>
<tr>
<td><strong>Detailed Models</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kang et al. (1997)</td>
<td>Peters and Rogg (1993), complex kinetics up to C₃, 32 species and 85 reactions</td>
<td>Propane</td>
<td>Temperature, soot volume fraction, soot number density and particle diameter, concentrations of intermediate species, soot zone thickness</td>
<td>Counter-flow, coflow and inverse coflow diffusion flames</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Reaction Scheme</td>
<td>Fuel</td>
<td>Variables Solved</td>
<td>Application</td>
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<td>---------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>Xu et al. (1997)</td>
<td>Detailed reaction kinetics up to C₆H₆ by Kazakov et al. (1995) and Leung</td>
<td>Ethylene</td>
<td>Mole fractions of intermediates as functions of C/O, soot particle surface growth rates</td>
<td>Laminar premixed ethylene/air flames at 1 atm</td>
</tr>
<tr>
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<td>and Lindstedt (1995) and references therein</td>
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</tr>
<tr>
<td>Kazakov and Frenklach (1998)</td>
<td>Detailed kinetics (HACA: hydrogen abstraction, carbon addition mechanism)</td>
<td>Ethylene</td>
<td>Soot number densities and volume fractions, extinction coefficient, volumetric scattering cross section</td>
<td>High pressure (10 bars) laminar premixed fuel/air flames</td>
</tr>
<tr>
<td>Du et al. (1998)</td>
<td>Ethylene and acetylene gas phase chemistry</td>
<td>Ethylene</td>
<td>Sooting limit and fuel molar fraction at various pressures (1 to 2.5 atm)</td>
<td>Counter-flow diffusion flames of nitrogen diluted fuel versus air</td>
</tr>
<tr>
<td>Dederichs et al. (1999)</td>
<td>PAH growth fast polymerization process (Mauss et al., 1994) and soot kinetics by Frenklach and Wang (1990)</td>
<td>Methane, acetylene, ethylene</td>
<td>Soot mass versus crank angle, soot volume fraction, contour plot of soot concentration</td>
<td>Diesel spray combustion, laminar or turbulent fuel/air jet flames</td>
</tr>
</tbody>
</table>
regarding soot yields at different process temperatures. In general though, the model was expected to underestimate soot growth rates as it neglected three dimensional growth and multiple attacks on the same growing nucleus.

This work was later on extended by Frenklach and Wang (1990) to a comprehensive soot model that also included coagulation of spherical particles in the free molecular regime, surface growth and oxidation. Aerosol dynamics calculations (for simultaneous nucleation, coalescent coagulation, and surface reactions) were based on the method of moments (Frenklach and Harris, 1987; Method II). More specifically, a van der Waals enhancement factor of 2.2 was used for the collision kernels while surface growth was considered by means of elementary reactions of active sites the density of which was dependent on the competition between H-abstraction/C$_2$H$_2$-addition (HACA) as well as O$_2$ and OH oxidation reactions. A typical surface reaction rate expression was given by the following formula:

$$r = k_g \cdot C_g \cdot \alpha \cdot \chi_s \cdot S \cdot N$$  

(1-1)

where $k_g$ was the per-site rate coefficient, $C_g$ was the concentration of the colliding species (i.e., H, C$_2$H$_2$, O$_2$, OH), $\chi_s$ was the density of active sites, S was the surface area of a given soot particle, N was the number concentration of this particle, and $\alpha$ was an empirical (adjustable) steric parameter corresponding to the fraction of active sites available for reaction. Model results (with respect to particle soot diameter, number and surface area concentration profiles) were in quantitative agreement with experiments in several laminar premixed (low pressure acetylene-oxygen and atmospheric ethylene-oxygen) flames. Soot reduced reactivity with increasing residence time was attributed (incorporating the HACA concept) to the decrease of H concentration (following a temperature descent by radiative heat losses) since H was needed to activate sites (either on PAHs or soot particle surfaces) for carbon addition.

Frenklach and Wang (1994) further modified the above model to account for soot particle optical properties such as scattering and extinction coefficients. Mauss and Bockhorn (1995) combined a fast polymerization process for PAH growth with a modified HACA scheme (including O$_2$ and OH oxidation) for heterogeneous surface reactions on soot particles. In addition, PAH - PAH and PAH - soot collisions were considered to follow Smoluchowski's coagulation equation. Reasonably good agreement was achieved between model predictions (with respect to soot volume fractions) and
experimental data in premixed stabilized ethene-air flames at pressures ranging from 0.1 MPa to 1.0 MPa. Finally, sensitivity analysis showed that the "pre-soot" gas phase reactions had the most important effect on the overall soot formation rates.

On an similar context, the work of Ivie and Forney (1988) remains one of the most characteristic efforts on the simulation of synthesis of carbon black particles. Their approach included formation of gaseous radicals from pyrolysis of benzene, nucleation of carbon particles, growth by coagulation and surface adsorption, and oxidation. According to the gas phase reaction scheme adopted (updated version of the gas phase kinetics scheme of Fujii and Asaba, 1977), phenyl radicals (C₆H₅) reacted with ring fracture products (C₂H₂, C₂H₃, C₄H₃) to form networks of aromatic rings. Stable carbon particles were formed when a biphenyl or phenyl radical grew to contain 14 carbon atoms, thus following the nucleation reaction:

\[ N\cdot y + n\cdot G\cdot x \rightarrow P\cdot z \]  \hspace{1cm} (1-2)

where N·y was the nucleating species containing y carbons (C₆H₅, C₁₂H₁₀), G·x was the growth species containing x carbons (C₂H₂, C₂H₃, C₄H₃) and P·z was a stable particle with \( z = 14 \) carbon atoms, thus \( n = (z - y)/x \). Stable carbon black particles grew bigger by coagulation and surface adsorption of growth molecules. This step was simulated with a sectional model of 10 size intervals arranged in such a way so that particles could only coagulate and grow into adjacent sections. Within a given section, four paths were assigned for particle gain while particle loss could take place in ten different ways. Collision frequencies were based on the Fuchs interpolation function (Seinfeld, 1986) while all particles were assumed to be spherical equivalents of the real aggregate structures. Oxidation reactions were considered both in the gas phase and on the surface of carbon black particles. Although in the gas phase the oxidation reaction scheme included, O₂, O, OH and HO₂ the burnout of carbon particles was assumed to proceed only by OH attacks the rate of which was calculated from kinetic theory. Decomposition of benzene and oxidation of C₆H₅ turned out to be the most sensitive reactions as fluctuations in their rate constants could remarkably affect particle nuclei concentration profiles. The differences between model predictions and experimental data for the mass average particle diameter, particle number concentration and CO concentration (+10 %, -18 % and -24 %, respectively) were attributed to uncertainties in the nucleation kinetics of phenyl radicals and omission of other possible particle surface oxidation agents such as oxygen radicals.
Lockwood and Van Niekerk (1995) carried out a parametric study regarding carbon black formation in a oil furnace using the same basic steps of formation and growth (namely, nucleation, surface reactions and coagulation) that were typically applicable to soot. For simplicity, they directly related the formation of soot to the concentration of the carbon black feedstock, rather than considering the prominent pyrolysis species of the parent fuel (Fairweather et al., 1992). More specifically, they applied the reduced mechanism of Stewart et al. (1991) distinguishing soot inception, surface growth and coagulation. Oxidation by hydroxyl radicals, aggregate structure irregularities and thermal radiation effects were neglected. In addition, the fuel-oxidant reaction was assumed fast while turbulence was simulated by the standard k/ε model. Radial and axial velocity components, static pressure, total enthalpy and species mass fractions were derived by solving the governing partial differential equations with a standard finite volume method. A set of experimental data (for a specific parent fuel) was used for calibration of model constants. It should be noted that for different feedstocks (in the absence of advanced chemical kinetics for pyrolysis of heavy aromatic fuels) recalibration of the model was necessary. The influence of geometric and fluid dynamics aspects (such as, process airflow, precombustor equivalence ratio, air temperature, and reactor volume) on the oil furnace operation was investigated by an extensive parametric analysis. In general, model results on particle specific surface areas (as functions of the air / feedstock ratio, carbon black production, specific fuel flow and yield) overpredicted the corresponding data reported in literature. Model prediction trends were however realistic. Finally, according to the authors, better model performance might have been achieved by using a more extensive source of data for calibration purposes.

1.3.3. Recent Advances in Soot Modeling

Kang et al. (1997) studied the sooting characteristics of counter flow, co-flow and inverse co-flow diffusion flames. Experimental evidence from soot particle light scattering-extinction measurements, PAH fluorescence and laser Doppler velocimetry, was further backed up by numerical analysis mainly accounting for the complex chemical kinetics (up to C₃) consisting of 32 species and 85 reactions (Peters and Rogg, 1993). Thermodynamic and transport properties were calculated from commercial software packages such as CHEMKIN (Kee et al., 1989) and TRANSOPRT (Kee and
Miller, 1983). It should be pointed out that the numerical approach adopted by Kang et al. (1997) did not consider the formation and oxidation of soot particles explicitly but only through the determination of pertinent important factors such as C\textsubscript{2}H\textsubscript{2}, OH and O\textsubscript{2} concentrations. This simplification however, was justified by the low sooting levels of the flames examined (less than 1 % fractional conversion of carbon atoms to soot). Results showed that soot particles moved towards the hot regions undergoing coagulation-growth and oxidation in co-flow flames and counter-flow flames located on the fuel side whereas in inverse co-flow flames and counter-flow flames located on the oxidizer side, soot particles simply "ran away" without experiencing oxidation. Finally, predictions of soot zone thickness in counter-flow diffusion flames were in reasonably good agreement with experimental measurements. The increase of C\textsubscript{3}H\textsubscript{8} concentration expanded the soot zone more drastically than the increase of O\textsubscript{2}.

Xu et al. (1997) used a variety of existing reaction mechanisms (Frenklach and Wang, 1990; Frenklach and Wang, 1994; Kazakov et al., 1995; Leung et al., 1991; Leung and Lindstedt, 1995) to investigate soot formation in atmospheric laminar premixed ethylene-air flames with C/O ratios ranging from 0.78 to 0.98 and soot concentrations up to ~ 1 ppm. More specifically, detailed reaction kinetics were employed up to C\textsubscript{6}H\textsubscript{6} involving either 250 elementary reversible reactions and 52 species (Frenklach and Wang, 1990; Frenklach and Wang, 1994; Kazakov et al., 1995) or 451 reversible reactions and 87 species (Leung et al., 1991; Leung and Lindstedt, 1995). Although these reaction schemes did not cover the complete range of mechanisms originally proposed by the above researchers, they were enough to estimate concentrations of major combustion species and other small radicals (for instance, OH, H, O). Thermophysical and transport properties such as multicomponent diffusion and thermal diffusion were calculated using PREMIX (Kee et al., 1985) while other additional process variables such as radiative heat losses were estimated by a series of in-house measurements. Irrespective of the reaction model chosen, the predicted mole fractions of major species such as C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, CO\textsubscript{2}, CO, H\textsubscript{2}O, H\textsubscript{2} and CH\textsubscript{4} as functions of C/O ratios were generally in good agreement with their experimental counterparts. In accordance with the HACA mechanism, soot growth rates diminished with residence time despite the continued presence of acetylene. This trend resulted from radiative heat losses, induced by the presence of soot particles, subsequently promoting the reduction of H radicals. Moreover, inception of soot primary particles was found to be first order
with respect to acetylene with an activation energy of 11,000 kJ/kg-mol. For reasons not explained, soot primary particle nucleation rates were nevertheless almost two orders of magnitude smaller than those in diffusion flames at similar conditions (Sunderland et al., 1995).

Ezekoye and Zhang (1997) investigated soot oxidation and aggregation in a microgravity spherical counter-flow acetylene-air diffusion flame. Gas phase reaction kinetics were based on a two-step global mechanism accounting for acetylene oxidation to CO and CO oxidation to CO\textsubscript{2}. Soot formation, aggregation, surface growth and oxidation by O\textsubscript{2} were modeled by combination of several existing schemes (Leung et al., 1991; Fairweather et al., 1992; Zhang and Ezekoye, 1996). Special attention was also given to OH oxidation (Moss et al., 1995). Reaction kinetics were coupled with the governing conservation equations for mass, gas phase species, gas phase sensible enthalpy, soot mass fraction and soot particle number density for unsteady, one dimensional (radial) diffusion. Thermodynamic and transport properties were evaluated by commercial software packages while gas and soot particle radiation effects were approximated by the spherical harmonics P1 approach. OH oxidation rates were found to be significantly larger than those of molecular oxygen. Aggregate and primary soot particle sizes were also larger than their corresponding counterparts in normal gravity flames. This behavior was attributed to longer residence times achieved in fuel enriched microgravity flames.

Kazakov and Frenklach (1998b) extended previous simulation efforts of soot formation and growth (Frenklach and Harris, 1987; Frenklach and Wang, 1994) to include dynamics of fractal aggregates all the way from the free molecular to the transition and continuum regimes. Their final objective was to develop a full-blown model describing detailed reaction kinetics for soot primary particle nucleation (Kazakov et al., 1995 and references therein), soot growth by coalescent-coagulation, aggregation and surface reactions, as well as soot mass loss by oxidation. In contrast to the free molecular regime, no van der Waals enhancement factor was used in the continuum while the Fuchs interpolation (Seinfeld, 1986) for the collision frequency function was approximated by a harmonic mean between the limiting cases of free molecular and continuum regimes. Such an approximation demonstrated maximum deviations from Fuchs' formula within 27%.
More specifically, simulations begun with gas phase chemical reactions up to pyrene based on the Sandia burner code PREMIX (Kee et al., 1985) and continued beyond pyrene with PAH growth and soot formation using a linear lumping scheme (Frenklach and Wang, 1994). Soot particle dynamics started with full coalescence, and switched later on to aggregation when a critical soot particle diameter $d^*$ (25 to 30 nm) was reached. Thereafter, aggregate structures were characterized by the so-called collision diameter which was used to replace particle diameters in the coagulation kernels following the approach of Kruis et al. (1993). Moreover, the accommodation of aggregate structures gave rise to binary moment terms $\langle m'n^r \rangle$ approximated (with an estimated error no larger than 20%) as:

$$\langle m'n^r \rangle = \sum_{i=1}^{\infty} m_i^n N_i \sum_{i=1}^{\infty} n_i^r N_i \frac{M_o}{M_o}$$

where $m_i$ and $N_i$ were respectively the mass and number densities of particles in the size increment $i$, $r$ was the moment order, $M_0$ was the zeroth moment equal to the total number of particles, $N$, and $n_i$ was the number of primary particles in the $i^{th}$ aggregate. In accordance with Kruis et al. (1993), each aggregate was characterized by a single primary particle size and had a mass fractal dimension $D_f$ of 1.8, where $D_f$ was defined as (Jullien and Botet, 1987):

$$n_p = k_f \left( \frac{2R_g}{d_p} \right)^{D_f}$$

where $n_p$ is the number of primary particles per aggregate, $k_f$ is constant called fractal prefactor, $R_g$ is the radius of gyration and $d_p$ the primary particle diameter. Finally, aggregate particle optical properties were appropriately modified by incorporation of the radius of gyration. In contrast to the extinction coefficient $k_{ext}$, the volumetric scattering cross section $Q_{vv}$ was significantly more sensitive to variations of $d^*$ and the fractal prefactor $k_f$. In general, the proposed model was able to predict the attainment of an asymptotic value for $N$ and gave results in good agreement with experimental data at high-pressure laminar premixed flames by adjustment of the latter parameters ($d^*$ and $k_f$).

Pressure effects on soot formation were studied by Du et al. (1998) in counter-flow diffusion flames of nitrogen-diluted ethylene versus air. Pressure was varied from
1 to 2.5 atmospheres. A series of experiments showing that the sooting tendency increased with pressure, led to an empirical correlation for the critical strain rate at the sooting limit, \( K_p \) (simply called sooting limit):

\[
\rho_o K_p \sim X_F^{0.5} p
\]

where \( \rho_o \) was the mass density of the cold oxidizer gas mixture, \( X_F \) was the molar fraction of ethylene in the fuel stream and \( p \) the pressure. Numerical analysis based on ethylene and acetylene gas phase chemistry revealed that the right hand side term of Equation 1-5 represented acetylene partial pressure at the critical sooting state, further indicating once again the dominant role of acetylene chemistry in soot formation and growth mechanisms.

Chao et al. (1998) developed a general model for soot inception in nonpremixed counter-flow flames focusing on hydrodynamics and transport effects. The simplified chemical reaction scheme proposed accounted for three steps: a) fuel oxidation (in the oxidation zone) to produce a final product and a radical species (for instance, H), b) soot/precursor inception (in the formation zone, next to the oxidation region) by reaction between the radical and the fuel and c) reaction between the soot/precursor and the oxidizer (in the consumption zone, next to the primary oxidation region) to produce more final product. Second order Arrhenius kinetics, unity fuel and oxidizer Lewis numbers (species and energy diffuse similarly), constant property potential flow, and faster soot/precursor formation than consumption were some of the basic assumptions-simplifications additionally adopted.

Solution of the governing energy and species conservation equations, with the application of the appropriate boundary conditions, yielded results on the flame temperature and location as well as the soot/precursor index which reflected the overall amount of soot/precursor at the boundary of the formation zone. Model predictions relevant to two limiting case studies (namely, the pure fuel - air and the diluted fuel - oxygen flames) were derived for process conditions close to ethylene/oxygen combustion. For pure fuel - air flames and in contrast to diluted fuel - oxygen flames, soot/precursor oxidation had virtually no effect on the amount of soot/precursor produced. It was also shown that low soot/precursor diffusion rates sustained high soot/precursor concentrations and decreased flame temperatures. In general, model results demonstrated, in agreement with previous experimental observations, that
modifications of the flame configuration could substantially affect soot/precursor concentrations.

Pressure effects on soot production rates were examined by Zhang and Ezekoye (1998) in a two-dimensional confined co-flow methane - air jet diffusion flame. Gas phase chemical reactions were represented by a reduced 8-step mechanism involving 12 major species. Similarly, soot kinetics were based on a reduced 4-step scheme (Fairweather et al., 1992) involving nucleation (using acetylene as the soot precursor species), surface growth, oxidation and aggregation. The governing equations for continuity, axial and radial momentum, chemical species, gas phase energy, soot mass fraction and soot particle number density were solved, in conjunction with a radiative field model, using a finite volume method. Model results were first validated by comparison with experimental data at atmospheric pressure (Mitchell et al., 1980). Both acetylene and soot were within 20 % of experimental values. Simulations at higher pressures (4 atm) revealed a decrease of soot particle number concentration, promoted by increased soot particle inception and aggregation rates. An interesting implication of this result was that combustion at elevated pressure conditions, (despite the larger soot mass output) could have considerably lower contribution to respiratory problems, in terms of production of bigger soot particles. Finally, another direct outcome was the increase of radiation heat transfer.

Dederichs et al. (1999) simulated soot formation and oxidation in Diesel spray combustion. They combined different CFD codes with detailed chemistry soot moment submodels involving gas phase chemical reactions, PAH growth as a fast polymerization process (Mauss et al., 1994), particle inception, surface growth, coagulation and oxidation (Frenklach and Wang, 1990). Flow calculations were uncoupled from combustion processes by use of a reduced flamelet library (formulating energy and species conservation equations for fast chemical reactions in a thin reaction zone, Peters, 1984) further modified to account for soot particle radiation heat effects, and incorporated in the soot model as a separate subroutine. Model predictions of soot volume fraction profiles were in good agreement with experimental data in a turbulent \( \text{C}_2\text{H}_4 \) - air jet flame. Furthermore, simulation results were generally in qualitative accordance with measurements of spatial soot mass distributions in spray combustion under Diesel engine conditions. Finally, it was pointed out, that better quantitative
comparisons could be achieved after incorporating detailed geometric effects in the simulations.

Hayashi et al. (1999) simulated Brownian cluster-cluster aggregation of soot particles formed by benzene pyrolysis in a furnace hot wall reactor. Soot primary particles grew to aggregates by collisions with other particles (or aggregates) after following random walks defined by their corresponding free mean paths. Aggregate structure was taken into consideration in terms of a volume equivalent diameter, $d_{eq}$, incorporated in the Stokes–Einstein diffusion coefficient $D$, along with a dynamic shape factor, $\kappa$ (Stöber, 1976):

$$D = \frac{kT}{3\pi\mu d_{eq}} \cdot \frac{C}{\kappa}$$  \hspace{1cm} (1-6)

with $k$ being the Boltzmann constant, $T$ the absolute temperature, $\mu$ the gas viscosity, and $C$ the slip correction factor (Hinds, 1999). In addition, $d_{eq} = n^{(1/3)}d_p$ and $\kappa = 0.86\cdot n^{(1/3)}$, with $d_p$ being the primary particle diameter and $n$ the number of constituent primary particles per aggregate. Average values of $d_p$ and $n$ were measured by electron micrographs of soot powders collected at the outlet of the furnace hot wall reactor. According to the proposed simulation scheme, a certain number of initially equal-sized single primary particles (of average $d_p$) was confined in a three dimensional space the size of which was a priori adjusted to match the actual particle number density (assuming that all the carbon content in the 1 mol % benzene became soot). Moreover, the initial number of primaries, $N_i$, was given by $n \cdot N_f$, where $N_f$ was the final number of aggregates. Growth of primaries in the above control volume proceeded by Brownian coagulation. Results with respect to aggregate shape, peripheral fractal dimension, and size distribution were in good agreement with their experimental counterparts. Finally, it was shown that for fixed process temperature but variable residence time, the peripheral fractal dimension was independent of the average number of primary particles per aggregate.

Smooke et al. (1999) combined a gas phase diffusion combustion model with soot chemistry and particle dynamics to simulate an axisymmetric laminar coflow diffusion flame. More specifically, the soot inception rate $S_i$ (g/cm$^3$/s) was given as (Hall et al., 1997):

$$S_i = 127 \times \frac{d[C_{10}H_7]}{dt} + 178 \times \frac{d[C_{14}H_{10}]}{dt}$$  \hspace{1cm} (1-7)
and was based on the assumption that oxidation/decomposition of polyaromatics could be neglected. Surface growth rates were derived from Harris and Weiner (1983) while oxidation by O$_2$ and OH was treated as in Hall et al. (1997). Particle dynamics (namely, soot nucleation, coalescent coagulation, surface growth and oxidation) were solved on a polydisperse sectional formulation basis (Hall et al., 1997) in conjunction with a set of transport conservation partial differential equations for radial and axial velocity, vorticity transport, species, and energy (including radiation effects). Numerical solution of spatial operators involved centered finite difference approximations (for diffusion terms) and upwind schemes (for convection). Poor agreement between experimental data and model predictions of flame heights, local temperatures and soot volume fractions, were attributed to uncertainties associated with the chemical mechanism adopted and burner boundary conditions. In qualitative accordance with earlier studies, simulation results revealed that soot net production was driven more by surface growth rather than by nucleation. In addition, it was shown that OH radicals played an important role in soot oxidation/burnout attaining high superequilibrium concentration levels while radiative heat losses decreased peak flame temperatures by over 100 K. Finally, substitution of the proposed soot inception/growth model with that of Fairweather et al. (1992) appropriately modified to account for OH oxidation, resulted in slightly higher soot volume fractions and different soot inception spatial distribution.

Kronenburg et al. (2000), introduced a conditional moment closure method (CMC) (Klimenko, 1995), as a new tool for simulation of soot formation in turbulent methane - air jet diffusion flames. Closure for the reaction rates was based on conditional averages rather than Reynolds or Favre averages, decoupling complex kinetics from nonuniformity or macromixing aspects of the flow (Bilger, 1993). Thus, in other words, conditional fluctuations on the mass fractions of most gaseous species were relatively smaller than their conditional means and did not have to be considered. Kinetic expressions were directly derived from semi-empirical soot models (originally developed for laminar diffusion flames) while soot inception and surface growth rates were expressed as first order functions of acetylene concentration. Additional modeling aspects involved O$_2$ and OH oxidation, soot particle aggregation, as well as CO$_2$, H$_2$O, CH$_4$ and soot thermal radiation effects. Good agreement was achieved with experimental measurements in flames under atmospheric or elevated pressure conditions. Oxidation mechanisms based on O$_2$ and OH radicals were shown to be
equally important while soot particle differential diffusion played a crucial role affecting the accuracy of soot loading model predictions by at least 40%. In general, the CMC formulation yielded better results than the laminar flamelet technique.

Kellerer et al. (2000) carried out measurements and theoretical calculations of soot particle coagulation in shock tubes at pressures ranging between 10 and 60 bars and process temperatures from 1500 to 2300 K. Particle dynamics for coalescent coagulation were solved in a discrete formulation by an in-house code. Collision frequencies were determined by the Fuchs interpolation function and dispersion forces effects were accounted for by the implementation of the van der Waals enhancement factor ($C_{ij}$). Soot particle nucleation rates were derived from light absorption measurements at the detection point of the first (monomer) particles. Freshly formed monomer soot particles were assumed monodisperse, 1 nm in diameter, with their number concentration estimated by the Rayleigh approximation. Surface growth rates were assumed proportional to particle surface area and were also determined experimentally.

Although calculated soot particle number concentrations were in good agreement with experimental values at the early stages (first 1 ms of particle growth), later on, when shifting from the free molecular to the transition regime, model predictions became substantially lower. Possible uncertainties concerning optical measurement parameters (namely, the refractive index, the particle size distribution and aggregate structure) were considered to have negligible effect. Furthermore, the use of a pressure and particle diameter dependent $C_{ij}$ could not explain, to the desired extend, the observed deviations. As a last resort, a variable sticking efficiency, $a$, was established to match both experimental results and theoretical calculations:

$$a = \exp(-t \cdot k_r) \text{ and } k_r = 2.0 \times 10^3 \exp\left[-\frac{(1900 - T)^2}{(260)^2}\right] \text{s}^{-1} \quad (1-8)$$

where $t$ was the particle lifetime and $T$ the absolute temperature. It was nevertheless concluded that additional particle dynamics calculations would be needed to shed more light on soot aggregate growth at elevated pressures.

Appel et al. (2000) extended the work of Kazakov and Frenklach (1998b) by updating the existing soot formation and growth kinetic model. Thus for instance, the detailed small-molecule gas phase chemistry was updated with new literature data, while PAH gas phase reaction schemes were augmented by the use of consistent
thermodynamic and transport properties and even expanded to adopt the hydrogen migration mechanism. Pyrene was the soot particle precursor whereas acetylene the principal surface growth species.

Predictions of the revised model were compared with experimental observations from nine laminar premixed flames of ethane, ethylene and acetylene (with the C/O ratios ranging from 0.6 to 1.3 and flame maximum temperatures varying from 1270 to 2100 K). Instead of using a constant surface-reaction steric multiplier, $\alpha$ (see equation 1), a new formulation was derived based on fitted parameters ($b$ and $c$):

$$\alpha = \tanh\left(\frac{b}{\log\mu_1} + c\right) \quad \text{with} \quad b = 12.65 - 0.00563 \cdot T, \quad b = -1.38 + 0.00068 \cdot T$$

where $\mu_1$ was the first size moment of the soot particle distribution. Although the model captured experimental soot volume fraction profiles reasonably well, particle diameters (for the majority of the cases studied) were significantly underestimated. Nevertheless, it should be mentioned that this performance was generally considered encouraging since results for a diversity of flames came from a single soot model.

1.4. AEROSOL DYNAMICS MODELING

1.4.1. Numerical Methods

In general, the most important mechanisms of particle formation and growth are monomer inception (that is nucleation or gas phase chemical reaction), coagulation, sintering and surface growth (or condensation). All these mechanisms are represented in the general dynamic equation (Kumar and Ramkrishna, 1997):

$$\frac{\partial n(v, t)}{\partial t} + \frac{\partial (G(v)n(v, t))}{\partial v} = \frac{1}{2} \int_0^v n(v', t)n(v' - v, t)q(v', v - v')dv'$$
$$- n(v, t) \int_0^v n(v', t)q(v, v')dv' + S(v)$$

(1-10)

where $n(v,t)$ is the particle density function of particles between $v$ and $v + dv$ at time $t$, $G(v)$ is the growth rate of particles of size $v$, $q(v,v')$ is the collision frequency between particles of sizes $v$ and $v'$ and $S(v)$ is the nucleation rate of particles of size $v$. The following section focuses on some of the most characteristic modeling efforts on combinations of the above mechanisms.
There are four basic types of models used in aerosol dynamics simulations: monodisperse, moment, discrete and sectional models. These are all numerical techniques arising from the lack of a general analytical solution of the dynamic equation (1-10). Monodisperse models neglect the spread of the particle size distribution by assuming particles or aggregates of equal size and describe, reasonably well, integral properties of the size distribution such as average particle size and total number concentration (Kruis et al., 1993; Panda and Pratsinis, 1995; Tsantilis et al., 1999; Tsantilis et al., 2001). They therefore constitute an attractive option in terms of simplicity and computational efficiency and can provide fast predictions for a number of aerosol applications. Figure 1-1, for instance, shows predictions of the monodisperse model of Tsantilis et al. (1999) regarding synthesis of bismuth (Bi) nanoparticles by simultaneous nucleation, condensation and coagulation in a jet aerosol flow condenser (Wegner et al., 2002). Particle diameters at the exit of the condenser (given as functions of the cooling rate and vaporization temperature, $T_v$ (K)) are in qualitative agreement with experimental data by Wegner et al. (2002).

![Flow in a Tubular Aerosol Condenser](image)

Figure 1-1: Bismuth particle diameters at the exit of a jet aerosol flow condenser (Wegner et al., 2002) as functions of the cooling rate and vaporization temperature, $T_v$ (K), using the monodisperse model of Tsantilis et al. (1999) for particle formation and growth by simultaneous nucleation, condensation and coagulation.
Typically, moment models describe the evolution of the moments of the aerosol size distribution (Kodas and Hampden-Smith, 1999) by approximating its shape, for instance as lognormal or self-preserving (Whitby, 1981; Landgrebe and Pratsinis, 1990; Megaridis and Dobbins, 1990). Their accuracy strongly depends on the validity of the above mentioned approximations (Fenklach and Harris, 1987). They provide information again on integral properties as well as general characteristics of the particle size distribution such as the standard deviation, skewness and kurtosis (Fenklach, 1985).

Discrete models provide the most accurate solutions to the detailed population balance equations but have considerable computational requirements (Fenklach and Harris, 1987). Sectional models require less computational power by discretizing the particle size distribution in a finite number of sections within which the size distribution density function remains constant. In addition sectional models can be combined with discrete schemes, especially when nucleation or birth of monomers by gas phase chemical reaction is to be taken into account (Wu et al., 1988, Rogak, 1997).

1.4.2. Coagulation with or without Gas Phase Chemical Reaction

Gelbard et al. (1980) proposed a general sectional representation for aerosol dynamics. They divided the particle size distribution into sections and dealt only with one average quantity (such as number, volume or surface area) in each section so that the corresponding moment (dependent variable) was consistent within the computational domain. The sizes of sections could be arbitrarily selected. However, some computational difficulties may arise with this method. For instance, for kernels that cannot be analytically integrated one may have to compute a large number of double integrals depending on the number of sections. Batterham et al. (1981) proposed a set of equations accounting for aggregation processes by considering the particle size distribution as truly discrete (only particles of volumes $\nu$, $2\nu$, $4\nu$, $8\nu$, $16\nu$ … could exist). Their method conserves mass but underestimates the total number and gives better results for longer rather than short residence times (Hounslow et al., 1988; Kostoglou and Karabelas, 1994).

Frenklach (1985) presented a mathematical approach based on the moments of the discrete particle size distribution function and provided an exact analytical solution of the discrete general dynamic equation for coagulation (Friedlander, 1977) and
particle independent coagulation kernels. Calculations of the time-lag for the attainment of an asymptotic distribution (for both monodisperse and polydisperse initial distributions) were also presented.

\[
\frac{dN_i}{dt} = (N_{i-1} \sum_{j=1}^{i-2} 2^{j-i+1} \beta_{i-1,j} N_j + \frac{1}{2} \beta_{i-1,i-1} N_{i-1}^2 - N_i \sum_{j=1}^{i-2} 2^{j-i} \beta_{i,j} N_j - N_i M \beta_{i,j} N_j)
\]

Figure 1-2: Number concentration of particles, \(N_i\) (cm\(^{-3}\)), in section \(i\) using the sectional model (for particle growth by coagulation) of Hounslow et al. (1988). The sectional discretization is fixed with a spacing factor \(f_s = \frac{v_{i+1}}{v_i} = 2\). The first RHS term refers to the rate of birth of particles in section \(i\) by collisions between particles of the \(i-1\) section and \(j\) sections ranging from 1 to \(i-2\). The second RHS term refers to birth of particles in the \(i^{th}\) section by collisions of equal size (\(i-1\)) particles. The third RHS term accounts for the death rate of particles in section \(i\) by collisions between these particles and smaller ones. The fourth RHS term corresponds to the death rate of particles in section \(i\) by collisions between these particles and particles in the same or higher size intervals.

Hounslow et al. (1988) chose the same fixed grid as that of Batterham et al. (1981). Their model is internally consistent with respect to the zeroth and third number-based moments of the size distribution and provides an excellent description of coalescent coagulation for both constant and size dependent collision kernels (sum kernels). The fact that this sectional formulation has a rather coarse grid (Figure 1-2) results to a small error of approximately 4% in the geometric standard deviation of the self preserving distributions as shown here in Figures 1-3 and 1-4, in agreement with earlier studies (Vemury et al., 1994b; Table 3). It should be mentioned that this model has been extended by Litster et al. (1995) to account for finer grids of certain type. Marchal et al. (1991) developed a sectional scheme that treats coagulation in a similar fashion as the chemical reaction between two species, while there is no limitation to the
relation between the sizes of consecutive sections. Their method conserves particle mass but underpredicts the total particle number.

![Graph](image)

**Figure 1-3:** Predictions of the self preserving (number based) geometric standard deviation, $\sigma_{gs}$, using the sectional model of Hounslow et al. (1988) (broken line), along with results from Vemury and Pratsinis (1995) (solid line) based on the refined sectional model of Landgrebe and Pratsinis (1990), for agglomeration in the free molecular regime and various mass fractal dimensions (Vemury and Pratsinis, 1995).

Kostoglou and Karabelas (1994), tested all the above mentioned sectional techniques for coalescent coagulation with constant and sum kernels. They concluded that the methods by Batterham et al. (1981) and Hounslow et al. (1988) are the most accurate. Furthermore, they stated that the method proposed by Hounslow et al. (1988) is more advantageous in terms of straightforward computer programming and fast program execution as well as in terms of mass conservation and consistency with the zeroth moment. Landgrebe and Pratsinis (1990), discretized the population balance equation paralleling the analysis of Gelbard et al. (1980) and Wu and Flagan (1988) and showed that coagulating aerosols truly approach self preserving size distributions in the free molecular and continuum regimes. This was later verified even for aggregate particles of various mass fractal dimensions (Vemury and Pratsinis, 1995).
Figure 1-4: Predictions of the self preserving (number based) geometric standard deviation, $\sigma_{gs}$, using the sectional model of Hounslow et al. (1988) (broken line), along with results from Vemury and Pratsinis (1995) (solid line) based on the refined sectional model of Landgrebe and Pratsinis (1990), for agglomeration in the continuum regime and various mass fractal dimensions (Vemury and Pratsinis, 1995).

Recently, Kumar and Ramkrishna (1996a) place particle populations at representative size intervals so that properties corresponding to two selected moments of the size distribution were exactly preserved (Figure 1-5). This technique does not require the evaluation of any double integrals but tends to overpredict the size distribution number density functions for coagulation in the size range (called front) where the number densities decrease steeply. Furthermore, the overprediction becomes more pronounced at longer times. Nevertheless, the authors state that a selective refinement of the grid in the size ranges containing "fronts" (fixed pivot technique) can substantially improve the accuracy of the numerical solution which is comparable to that of the sectional model of Hounslow et al. (1988) with the same degree of refinement (Litster at al., 1995). It should be mentioned though that the grid in the method of Litster et al. (1995) cannot be selectively refined, since the relation between consecutive sections is not arbitrary.
Particle population in \(i\)-th volume size interval is represented by a pivot \(x_i\).

Incoming particles are assigned to adjacent pivots preserving two or more moments.

Figure 1-5: Summary of the basic features of the (fixed pivot) sectional model of Kumar and Ramkrishna (1996a).

Kumar and Ramkrishna (1996b) further improved the fixed-pivot model to a moving-pivot one where the variations of the number density function were monitored through the location of a moving pivot that represented the population of the corresponding size range. In conclusion, they stated that the moving-pivot technique could make very accurate predictions even with a grid twice as course as the one used in the fixed-pivot scheme.

1.4.3. Coagulation of Non-Spherical Particles (Coagulation and Sintering)

The introduction of sintering does not influence the aggregate particle volume but its surface area. Simulation of aggregate particle morphology therefore requires the extension of the one-dimensional population balance problem (Equation 1-10) to a two-dimensional one (that is, the population density function is now function of both volume and surface area). Koch and Friedlander (1990) introduced an elegant model describing particle growth by coagulation and sintering. Their model predicted average primary particle sizes but neglected the effect of aggregate structure on the collision rate by assuming that aggregates collided at the same rate as spherical particles of equal volume. Xiong and Pratsinis (1993) developed an elaborate two dimensional sectional
model incorporating the effect of sintering (Koch and Friedlander, 1990) to the population balance equation. Their model traced particle volume and surface area evolution for coagulation and sintering from the free molecular to the continuum regime. They related the accessible surface area of an aggregate to its volume through a constant scaling factor and compared model predictions with experimental data on silica, titania and even boron carbide (Xiong et al., 1993; Weimer et al., 1991).

A simple monodisperse model to describe the particle morphology, size and number concentration by coagulation and sintering was proposed by Kruis et al. (1993). In this model the radius of gyration was implemented as the collision radius of aggregates of constant mass fractal dimension. Regarding the primary particle diameter, the model predictions were in agreement, at certain cases, with sectional (Xiong and Pratsinis, 1993), self preserving (Koch and Friedlander, 1990) models and experimental data on silicon formation.

Akhtar et al. (1994) developed a Monte Carlo simulation to describe coagulation and sintering of two dimensional particles. They accounted for particle restructuring through energy minimization, and showed the time evolution of the cluster mass fractal dimension. More specifically, their simulations showed a rather exponential decay of the mass fractal dimension with respect to Monte Carlo time steps (Akhtar et al., 1994: Figure 8). In addition, the mass fractal dimension seemed to decrease more steeply for low rather than high sintering rates. At longer Monte Carlo times though, mass fractal dimensions, for both slow and fast sintering, approached a constant value of 1.55 corresponding to that dictated by cluster-cluster aggregation of 2-dimensional particles (also equivalent to $D_f = 1.8$ for 3-dimensional particles (Seto et al., 1997)).

Vemury et al. (1994) addressed simultaneous coagulation and sintering by solving the population balance equation using the technique of Hounslow et al. (1988). The aggregate structure was taken into consideration by the implementation of a constant mass fractal dimension of 1.8 on the aggregate collision volume. They showed that experimental data (Xiong et al., 1993) could be better explained with this formulation and a modified sintering rate as they could distinguish between primary and aggregate particle size distributions.

Rogak (1997) extended the discrete sectional formulation by Wu and Flagan (1988) to study primary particle formation by coagulation with rapid coalescence and condensation-like growth. He assumed instantaneous sintering for particles below some
size “Dmeht” and birth of primary particles above this critical size. His model showed that primary particle diameters were less temperature dependent than would be expected from existing sintering models.

Very recently, Tsantilis and Pratsinis (2000) developed a simplified version of the two dimensional sectional formulation of Xiong and Pratsinis (1993) based on the fixed discretization scheme of Hounslow et al. (1988). A representative aggregate was assigned on the midpoint of each volume interval with an average, but variable with time, surface area. Aggregate and primary particle size distribution profiles were thus calculated in a computationally efficient manner. Model predictions were in fairly good agreement with experimental data (Akhtar et al., 1991) and other more detailed and computationally intensive sectional and discrete sectional models (Xiong et al., 1993; Rogak, 1997, respectively).

1.4.4. Coagulation (of Spherical Particles) and Surface Growth

Of particular interest is the investigation of the competition between gas phase and surface reaction mechanisms during particle formation and growth. Frenklach and Harris (1987) presented an alternative approach of the evolution of the moments of the size distribution avoiding the typical requirement of a-priori knowledge of the population density function (PDF). The accuracy of the proposed model was tested by comparisons with a discrete formulation for the case of coagulation as well as simultaneous particle nucleation, coagulation and surface reaction of soot (Frenklach et al., 1984). The spacing factor was $f_i = (1 + 1/i)$ for $i = 1… 10,000$. (It should be noted here that there is no problem of numerical diffusion in a fully discrete scheme, however, in a sectional model, numerical diffusion deteriorates, at the expense of computational efficiency, only for very refined discretizations (Warren and Seinfeld, 1985)). The proposed moment model was either based on approximations of the collision kernels (Method I) or on interpolation techniques for the evaluation of the time derivatives of the moments (Method II). For narrow particle size distributions method I was fairly accurate while Method II was in general more precise with its accuracy depending on the moment order and interpolation method used.

Pratsinis and Spicer (1998) studied the effect of TiCl₄ surface reaction (that is oxidation of TiCl₄ on the surface of already existing TiO₂ particles) on the size of product titania (TiO₂) particles over a wide range of process conditions. They developed
a monodisperse model and showed, for the first time, that TiCl\textsubscript{4} surface oxidation is more important (compared to gas phase oxidation) at high TiCl\textsubscript{4} initial concentrations.

Spicer et al. (2002) extended this work by carrying out calculations with a moving sectional population balance model (Kumar and Ramkrishna, 1997) (Figure 1-6). They predicted that when the surface reaction pathway was significant, it narrowed the particle size distribution, which nevertheless reached the self-preserving limit for coagulation at long residence times. Monodisperse and sectional calculations were also in good agreement for fast chemical reactions. Recently, Pratsinis et al. (2000) studied synthesis of titania particles from titanium-tetraisopropoxide (TTIP) in a premixed flat flame. They used the monodisperse model of Pratsinis and Spicer (1998) to derive an effective surface reaction rate of TTIP on TiO\textsubscript{2} particles and explain the evolution of experimental primary particle diameters at different locations along the flame (just few millimeters from the burner tip, all the way up to the filter, 20 cm away).

\[
\frac{dx_i}{dt} = \frac{1}{2} (V_i + V_{i+1})
\]

\[
x_{i+1} = 2 \cdot x_i
\]

*Figure 1-6: Pivots, \(x_i\), in the model of Kumar and Ramkrishna (1997) for simultaneous surface growth and coagulation, have to move to avoid numerical dispersion.*

Finally, it should be mentioned that Tsantilis et al. (2002) have recently developed sectional and monodisperse models accounting for simultaneous surface growth and sintering mechanisms in a straightforward manner. To the best of our knowledge, this is so far the only model available combining the above effects. The moment method of Kazakov and Frenklach, 1998b, discussed earlier, did not deal with
finite sintering times but with the extreme cases of either full coalescence or pure aggregation. Furthermore the switch from the former to the latter case took place at a critical particle diameter which was experimentally determined.

1.5. CONCLUSIONS

The present review focused on the latest advances in soot formation and growth modeling, mainly covering a time period of four to five years following the major review of Kennedy, I. M., on the same subject in 1997. Typical comprehensive modeling efforts include gas phase chemistry, (poly)aromatic ring growth, soot particle inception, coagulation (or even aggregation), surface growth and oxidation basically by \( \text{O}_2 \) and \( \text{OH} \) radicals. In contrast to particle dynamics representations that have already evolved into robust (monodisperse, moment, sectional and discrete sectional) formulations, soot chemistry is still an area governed by many uncertainties. So far, reaction schemes proposed by Frenklach and co-workers, incorporating the so called hydrogen abstraction, carbon addition (HACA) model, have become the "bread and butter" of detailed soot kinetics. Reduced reaction mechanisms could also become attractive, especially when dealing with complex fluid dynamics and turbulence.

The majority of modeling efforts associated with soot particle dynamics is based on moment and sectional methods with an almost clear preference to the former numerical techniques. This could be attributed to the additional complexity and computational demands (with some exceptions of course) of sectional schemes. Monodisperse models could also play an important role mainly because of their descriptive simplicity, computational efficiency and straightforward applicability. Although computational power is a persisting limiting factor in many applications, current trends, both in industrial and academic environments, involve solution of full-blown soot formation problems in conjunction with CFD packages, thus closely reflecting the intricate process conditions of diesel engines or commercial combustors in general. It should be pointed out, nevertheless, that purely experimental approaches remain in the vanguard of soot research.

Finally, when considering the more realistic case of surface growth in conjunction with particle shape irregularities, an alternative approach could be the combination of empirical or semi-empirical models of soot inception, surface growth and oxidation with monodisperse calculations accounting for simultaneous chemical
reactions, coagulation and sintering. Such an effort could provide useful tools to build-up knowledge on several aspects of soot formation relevant to the conditions of special interest, and could be later on used as a steppingstone to more elaborate simulation formulations.

1.6. REFERENCES


2. SINTERING TIME FOR SILICA PARTICLE GROWTH

ABSTRACT

The formation and growth of gas-made silica particles by coagulation and sintering is investigated theoretically. A model for the characteristic time for silica sintering is proposed defining a minimum primary particle diameter above which macroscopic expressions are applied. The value of the minimum primary particle diameter is selected consistently with molecular dynamics simulations. The proposed characteristic sintering time is tested using a monodisperse model for aggregate dynamics by coagulation and sintering. The model predictions are compared with experimental data for silica formation and growth in premixed flames and hot wall aerosol flow reactors by oxidation of hexamethyl-disiloxane (HMDSO) and silicon-tetrachloride (SiCl₄).

2.1. INTRODUCTION

Simultaneous coagulation and sintering is the main mechanism for aerosol formation and growth during flame synthesis of fumed silica (Ulrich, 1971) and even of titania (Xiong and Pratsinis, 1991) especially at dilute precursor concentrations (Pratsinis and Spicer, 1998). Depending on the application, the desired product may be in the form of non-aggregate or aggregate powders. For example, non-aggregate powders are desired in pigments and cosmetics while aggregate particles of high specific surface areas are required in reinforcing, photocatalysis and catalysis in general (Pratsinis, 1998). Quantitative understanding of aggregate formation is therefore important for the scale-up of experimental set-ups as well as the optimization of industrial process conditions.

Ulrich and Subramanian (1977) described the evolution of primary particles by coalescence of flame generated aggregates. Koch and Friedlander (1990) introduced a sintering model accounting for particle growth by coagulation and sintering in the free molecular regime assuming that aggregates collided at the same rate as spherical particles of equal volume. Xiong and Pratsinis (1993) developed a detailed two-dimensional
sectional model incorporating the effect of sintering to the population balance equation. Their model traced particle volume and surface area evolution by coagulation and sintering from the free molecular to the continuum regime. They compared model predictions with experimental results on silica, titania and even boron carbide (Xiong et al., 1992; 1993). They attributed the deviation of their model from experimental data to the uncertainty on the sintering time of very small primary particles, typically detected at the very early stages of aerosol formation. A simple monodisperse model describing particle morphology, size and number concentration by coagulation and sintering was proposed by Kruis et al. (1993). In this model the radius of gyration was implemented as the collision radius of aggregates of constant mass fractal dimension. The model predictions were in agreement, in certain cases, with sectional (Xiong and Pratsinis, 1993), self-preserving (Koch and Friedlander, 1990) models and experimental data on silicon formation. Akhtar et al. (1994) developed a Monte Carlo simulation to describe coagulation and sintering of two-dimensional particles. They accounted for particle restructuring through energy minimization, and showed that sintering delays the attainment of constant fractal dimension by the colliding clusters.

Seto et al. (1995) studied sintering of titania aggregates of nanosized primary particles from room temperature to 1673 K. They solved the basic equation for aggregate surface area depletion by sintering (Koch and Friedlander, 1990) and explained the experimentally observed results of aggregate densification and primary particle growth within the range of 1000-1500 K. Seto et al. (1997) extended their study by employing a two-dimensional sectional technique (Xiong and Pratsinis, 1993) for sintering of polydisperse titania and silica aggregates and found that primary particles coalesced at temperatures that were 50 % - 100 % of the bulk melting points of the corresponding particle material. Their experimental data for the sintering rates of silica and titania were in agreement with Xiong et al. (1993) and Kobata et al. (1991), respectively.

Lehtinen et al. (1996) proposed an equation for the dimensionless excess area of aggregates and determined the effect of sintering based on the difference between collision and coalescence times. When those two times were equal, dendrites were formed while the constituent primary particles stopped growing. The effect of process variables such as
temperature, velocity and volume loading on the size of primary particles in turbulent gas flows in a pipe and turbulent round free jets were also studied. Rogak (1997) extended the discrete sectional formulation by Wu and Flagan (1988) to study primary particle formation by coagulation with rapid coalescence and condensation-like growth. He assumed liquid-like particles that coalesced instantly below some size “$D_{\text{melt}}$” and birth of primary particles above this critical size. A first approximation of $D_{\text{melt}}$ could be given by the comparison between the characteristic time for sintering and particle residence time. He observed that a value of 1 nm for $D_{\text{melt}}$ could result in primary particle diameters consistent with measurements of Wu et al. (1993) on formation and growth of alumina aggregates under conditions of fast precursor reaction. His approach also showed that primary particle diameters were less temperature dependent than would be expected from existing sintering models.

Martinez-Herrera and Derby (1995) employed a two-dimensional finite element model in order to study the effects of initial particle size distribution and configuration on viscous sintering of spherical particles. They reported that greater neck-to-particle ratios resulted in faster overall shrinkage. Zhou and Derby (1998) developed a three-dimensional finite element model implemented on a massively parallel supercomputer. Their calculations predicted asymmetric neck growth resulting in particle rearrangement and anisotropic shrinkage. Mainly investigating the formation of composite silica/titania particles, Ehrman et al. (1998) also tried to simulate their experimental results of synthesis of pure titania or silica, using the model by Koch and Friedlander (1990). While getting good results for titania, the approach failed for silica. Recently, Xing and Rosner (1999) proposed a modification to the coalescence rate of nanoparticles that sinter by surface diffusion, by considering a curvature-dependent barrier for the surface diffusion activation energy. They compared their new sintering times with characteristic collision times, for Brownian coagulation of particle populations following self-preserving size distributions in the free-molecular regime, to predict primary particle sizes above which aggregate formation occurred. Their predictions were also in good agreement with experimental data on Al$_2$O$_2$ and TiO$_2$ particle formation by fast precursor reactions.
Differences between theory and experiments may arise from the implementation of bulk material properties for the derivation of characteristic sintering times of nanostructured particles. The objective of the present study is to introduce a sintering model for silica which holds for different experimental systems and is based on property data. Simulations with the model by Kruis et al. (1993) are carried out for a variety of conditions (Briesen et al., 1998; Seto et al., 1997; Ehrman et al., 1998). The predictions of the model are also compared to simulations using previous characteristic sintering times.

2.2. THEORY

2.2.1. Aerosol Dynamics Model

Particles in aerosol processes are typically formed by chemical reaction, coagulation and sintering in the absence of a nucleation barrier and surface growth as for instance, in synthesis of fumed silica (Ulrich, 1971). Though there is a plethora of models describing aerosol coagulation and sintering, here a monodisperse model (Kruis et al., 1993) is employed for simplicity. The experimental systems to be considered here refer to either premixed flames (Briesen et al., 1998; Ehrman et al., 1998) or furnace tube (hot-wall) reactors (Seto et al., 1997). According to the model by Kruis et al. (1993), the particle number concentration, \( N (\text{# particles/g}_{\text{gas}}) \), decreases by coagulation as follows:

\[
\frac{dN}{dt} = -\frac{1}{2} \beta N^2 \rho_g
\]  

(2-1)

where \( \rho_g \) (g/cm\(^3\)) is the gas density and \( \beta \) (cm\(^3\)/s) is the collision frequency function for Brownian monodisperse coagulation given by the Fuchs interpolation function from the free-molecular to the continuum regime (Seinfeld, 1986). The effect of aggregate structure in \( \beta \) is incorporated by replacing the primary particle diameter with the so-called collision diameter (Kruis et al., 1993). A constant mass fractal dimension, \( D_f \), of 1.8 is also used which is common for aggregate particles generated by cluster-cluster aggregation in high temperature aerosol processes (Schaefer and Hurd 1990). The rate of change of the average aggregate particle volume \( v \) (cm\(^3\)) is:
while the rate of change of the average aggregate particle area, $\alpha$ (cm$^2$), is:

$$\frac{d\alpha}{dt} = -\frac{1}{N} \frac{dN}{dt} \alpha - \frac{1}{\tau_s} (\alpha - \alpha_s)$$  \hfill (2-3)$$

where $\alpha_s$ is the surface area of a completely fused (spherical) aggregate of volume $v$, and $\tau_s$ (s) is the characteristic sintering time (time needed to reduce by approximately 63% the excess surface area of an aggregate over that of an equal mass sphere (Xiong and Pratsinis, 1993)). Equation 2-3 shows that the surface area of an aggregate particle increases by coagulation (first right-hand-side, RHS, term) and decreases by sintering (second RHS term). The primary particle diameter, $d_p$ (cm), and number of primary particles per aggregate, $n_p$, are given by:

$$d_p = \frac{6v}{\alpha}$$ \hfill (2-4)$$

$$n_p = \frac{\alpha^3}{36\pi v^2}$$ \hfill (2-5)$$

The characteristic sintering time of silica based on a viscous flow mechanism was determined by Xiong et al. (1993) using Frenkel's (1945) equation and silica property data by Kingery et al. (1976):

$$\tau_{s,X} = 6.5 \times 10^{-15} d_p \exp\left(\frac{8.3 \times 10^4}{T}\right)$$ \hfill (2-6)$$

where $T$ (K) is the process temperature. Recently, Ehrman et al. (1998) calculated the characteristic sintering time of silica, for viscous flow, from property data accounting for the effect of hydroxyl groups (Hetherington et al., 1964):

$$\tau_{s,E} = 6.3 \times 10^{-10} d_p \exp\left(\frac{6.1 \times 10^4}{T}\right)$$ \hfill (2-7)$$

Equations 2-1 – 2-3 can be further transformed as follows:

$$\frac{dF}{dt} = \frac{dF}{dx} \frac{dx}{dt} = \frac{dF}{dx} u_s$$ \hfill (2-8)$$

where $F = N, v, \alpha$
\[ u_x = \frac{Q_o \cdot T(x)}{60 \cdot S \cdot T_o} \]  

(2-9)

where \( u_x \) (cm/s) is the gas velocity, \( T_o \) (K) is the gas reference temperature, \( Q_o \) (cm\(^3\)/min) is the gas flowrate at reference conditions (1 atm, 298 K), \( S \) (cm\(^2\)) is the cross sectional surface area of the flow, and \( T(x) \) the process temperature profile. Equations 2-1 – 2-3 are solved by DGEAR software (IMSL, 1980) with the initial conditions (\( x = 0 \) cm): \( N = N_o, v = v_o, \alpha = \alpha_o \), where \( N_o \) is the initial monomer (molecule) concentration of SiO\(_2\), and \( v_o, \alpha_o \) are the equivalent-sphere volume and surface area, respectively, of a silica molecule.

2.2.2. New Characteristic Sintering Time

The numerator of the exponential factor in Equations 2-6 and 2-7 is proportional to the activation energy, \( E_{\text{bulk}} \) (J/mol), of viscous flow (Frenkel, 1945) for sintering of SiO\(_2\) particles. The viscosity of liquids, \( \mu \) (g·cm\(^{-1}\)·s\(^{-1}\)) can be expressed in general by an Arrhenius-type term (Kingery et al., 1976; Reid et al., 1987):

\[ \mu = A \cdot \exp \left( \frac{E_{\text{bulk}}}{R \cdot T} \right) \]  

(2-10)

Equation 2-10 however does not account for the effect of particle size. Similarly to Xing and Rosner (1999), such an effect could be accounted for by extending the particle size dependence of the melting point of metals (Buffat and Borel, 1976) to silica:

\[ \frac{T_{m,\text{particle}}}{T_{m,\text{bulk}}} = 1 - \frac{4}{L \cdot \rho_s \cdot d_p} \left( \sigma_s - \sigma_f \left( \frac{\rho_s}{\rho_l} \right)^{\delta_0} \right) \]  

(2-11)

where \( T_{m,\text{particle}} \) and \( T_{m,\text{bulk}} \) (K) are the melting points of the material in the particle and bulk phase, respectively, \( L \) (erg·g\(^{-1}\)) is the latent heat of fusion, \( \rho_s \) and \( \rho_l \) (g/cm\(^3\)) are the solid and liquid densities and \( \sigma_s \) and \( \sigma_f \) (erg·cm\(^{-2}\)) are the solid and liquid surface tensions. The values of \( \rho_s, \rho_l, \sigma_s, \sigma_f, \) and \( L \) correspond to properties of the bulk material at the melting point (Buffat and Borel, 1976). Equation 2-11 neglects the effect of particle size on liquid and solid surface tensions. For liquid droplets such an effect could be accounted for by the Tolman equation (Tolman, 1949) incorporating the ratio \( \delta/\delta_0 \) (\( \delta \) is a constant of the order
of intermolecular distance, ~ 0.1 nm) and which, in lack of available data for silica, can be neglected as it is typically very small. Furthermore, $\sigma_s$ is relatively insensitive to particle (cluster) diameter as shown by Zachariah and Carrier (1996; 1999) studying the dynamics of silicon (Si) clusters of up to 450 atoms.

The second RHS term of Equation 2-11 is further simplified by grouping terms:

$$\frac{T_{m,particle}}{T_{m,bulk}} = 1 - \frac{d_{p,min}}{d_p} \tag{2-12}$$

where $d_{p,min} = \left(\frac{4}{(L \cdot \rho_s)}\right)\left(\sigma_s - \sigma_i \left(\rho_s / \rho_i\right)^{\frac{1}{3}}\right)$ for $d_p > d_{p,min}$. Based on Equation 2-10 and assuming that the viscosity of the bulk material at the melting point temperature, $\mu_{bulk}(E_{bulk}, T_{m,bulk})$, equals that of the particle, $\mu_{particle}(E_{particle}, T_{m,particle})$, one can obtain a correlation for the dependence of the viscous-flow activation energy on particle size. Thus:

$$E_{particle} = E_{bulk} \frac{T_{m,particle}}{T_{m,bulk}} = E_{bulk} \left(1 - \frac{d_{p,min}}{d_p}\right) \tag{2-13}$$

where $E_{particle}$ and $E_{bulk}$ (J/mol) are the activation energies corresponding to the particle and bulk material, respectively. The assumption, $\mu_{particle} = \mu_{bulk}$, is in agreement with recent molecular dynamics studies showing that at moderate to high temperatures, the thermophysical properties of the particles are close to those of the bulk material (Zachariah et al., 1996; Zachariah and Carrier, 1999). In addition, it should be noted that the preexponential factor, $A$, in Equation 2-10 is the viscosity at high temperature. Consequently, as long as $\mu_{particle} = \mu_{bulk}$, $A_{particle} = A_{bulk} = A$.

Equations 2-6 or 2-7 can be now modified by introducing the above correction factor for the activation energy term. Thus for instance, Equation 2-6 becomes:

$$\tau_s = 6.5 \times 10^{-15} d_p \exp\left(\frac{8.3 \times 10^4}{T} \left(1 - \frac{d_{p,min}}{d_p}\right)\right) \tag{2-14}$$

Significantly low melting point temperatures and viscous flow activation energies are achieved for particle diameters very close to $d_{p,min}$ (Equations 2-12 and 2-13). This is an
indication of virtually no barrier for sintering of particles in that size range. Therefore, sintering could be practically assumed instantaneous for \( d_p \leq d_{p,\text{min}} \).

Here, \( d_{p,\text{min}} \) does not depend on temperature. This could be sustained only by very small particle sizes where a less strongly bound surface is dominant (with respect to cluster topography and not necessarily total binding energy) over a restricted more tightly bound core (Zachariah et al., 1996; Sheka et al., 1999). Indeed, the smaller is the cluster size, the more insensitive its sintering time becomes to wide temperature variations (Zachariah and Carrier, 1999). Furthermore, tiny particles witness upon collision a remarkable local and temporary temperature built-up, (Zachariah and Carrier, 1999) that could considerably boost full coalescence.

Detailed molecular dynamics studies elucidate the twofold nature of nanoparticles (neither solid, nor liquid, Preining, 1998) and could be set, in lack of available property data for silica, as a useful background for determining \( d_{p,\text{min}} \). As a first approximation, a critical particle diameter of 1 nm is selected corresponding to a cluster of approximately 12 silica molecules. This value is in agreement with molecular dynamics simulations for Si particles showing that at a cluster size of approximately 10 – 20 atoms the sharp decrease in the ratio of surface to bulk binding energy is almost complete (Zachariach et al., 1996; Fig 10). This value of \( d_{p,\text{min}} \) is almost 2.3 times the volume equivalent molecular diameter of SiO\(_2\). The value of 2.3 is also the ratio Rogak (1997) found for alumina (which has almost the same volume equivalent molecular diameter as silica) to predict primary particle diameters consistent with the experiments by Wu et al. (1993) under conditions of fast precursor reaction. In addition, the corresponding \( d_{p,\text{min}} \) for gold is around 2 times its volume equivalent molecular diameter (Buffat and Borel, 1976) which is close to our ratio of 2.3. The value of \( d_{p,\text{min}} = 1 \text{ nm} \) will be used here only as a first approximation of the actual \( d_{p,\text{min}} \). Finally, since \( d_{p,\text{min}} \) is defined as the diameter up to which sintering instantly takes place, for \( d_p \leq d_{p,\text{min}} \) Equation 2-3 has to be replaced by:

\[
\alpha = \alpha_0 \left( \frac{N_0}{N} \right)^{\frac{1}{2l}}
\]

(2-15)

which corresponds to full coalescence among particles.
2.3. RESULTS AND DISCUSSION

First, the proposed model is compared with experimental data for synthesis of silica in a premixed CH\textsubscript{4} / O\textsubscript{2} / N\textsubscript{2} flame (Briesen et al., 1998). The initial precursor flowrates (SiCl\textsubscript{4} or Hexamethyldisiloxane - HMDSO) can be calculated by the ratio of silicon atom to methane delivery rate \( \chi \) (Briesen et al., 1998; Equation 5) and the reported saturation (approximately 60 %). To facilitate computations the recorded temperature data were cast into a continuous profile by interpolation through:

\[
T = T_o + T^* \cdot \left( \exp\left( \frac{-x}{s_c} \right) - \exp\left( \frac{-x}{s_h} \right) \right)
\]  

(2-16)

\[ \text{(Figure 2-1: Comparison of experimental temperature profiles (symbols) with results from Equation 2-16 (lines) for two different total gas flowrates through a premixed burner.)} \]

Figure 2-1 shows a comparison between experimental temperature profiles and Equation 2-16 for two different total gas flowrates. Since the flame temperatures in Briesen et al. (1998) were measured with a thermocouple in the absence of precursor the temperature
profiles (Equation 2-16) were scaled according to the calculated adiabatic flame temperatures in the absence ($T_a$) and presence ($T_{a,prec}$) of precursor:

$$T = \frac{T_{a,prec}}{T_a} \left[ T_o + T^* \cdot \left\{ \exp\left(\frac{x}{s_c}\right) - \exp\left(\frac{x}{s_h}\right) \right\} \right] \quad (2-17)$$

For decomposition of HMDSO ((CH$_3$)$_6$Si$_2$O), the initial SiO$_2$ concentration is calculated assuming fast and complete reaction (Ehrman et al., 1998).

$$r_{HMDSO} = -k_o \cdot \exp(-E/(RT)) \cdot C_{HMDSO} \quad (2-18)$$

where $k_o = 4 \times 10^{17}$ s$^{-1}$, $E = 370 \times 10^3$ J/mol, $R = 8.314$ J·mol$^{-1}$·K$^{-1}$ and $C_{HMDSO}$ is the HMDSO concentration (mols/g$_{gas}$). According to Equation 2-18, the high temperatures encountered close to the burner face lead to a complete conversion of HMDSO almost within the first millimeter, for all conditions listed in Table 2-1.

### Table 2-1: Interpolation parameters and adiabatic temperatures for precursor free ($T_a$), HMDSO ($T_{a,H}$) and SiCl$_4$ ($T_{a,S}$) laden flames for various flows of the premixed flames of Briesen et al. (1998).

<table>
<thead>
<tr>
<th>Total Flow (cm$^3$/min)</th>
<th>$T^*$ (K)</th>
<th>$s_c$ (cm)</th>
<th>$s_h$ (cm)</th>
<th>$T_a$ (K)</th>
<th>$T_{a,H}$ (K)</th>
<th>$T_{a,S}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5350</td>
<td>1535.5</td>
<td>7.30</td>
<td>0.056</td>
<td>1896</td>
<td>1979</td>
<td>1896</td>
</tr>
<tr>
<td>5450</td>
<td>1486.1</td>
<td>6.97</td>
<td>0.063</td>
<td>1876</td>
<td>2048</td>
<td>1876</td>
</tr>
<tr>
<td>5550</td>
<td>1472.8</td>
<td>6.69</td>
<td>0.069</td>
<td>1855</td>
<td>2107</td>
<td>1854</td>
</tr>
<tr>
<td>5650</td>
<td>1432.1</td>
<td>6.30</td>
<td>0.077</td>
<td>1837</td>
<td>2163</td>
<td>1833</td>
</tr>
<tr>
<td>5750</td>
<td>1402.5</td>
<td>6.05</td>
<td>0.084</td>
<td>1817</td>
<td>2217</td>
<td>1815</td>
</tr>
</tbody>
</table>

Figure 2-2a shows the temperature profile (Equation 2-17) along with the evolution of silica primary particle diameter from the burner face as calculated by Equations 2-1 - 2-3 using the sintering time, $\tau_{s,X}$ (Equation 2-6) for HMDSO initial concentration of $5.93 \times 10^{-5}$ mol/g$_{gas}$ and a total gas flowrate, $Q_o$, of 5550 cm$^3$/min. It is clear that the primary particle
diameter slightly increases only at high temperatures. It should be noted however, that $\tau_{s,X}$ can give results in good agreement with experimental data for sintering of relatively bigger particles, $d_p > 10\,\text{nm}$ (Seto et al., 1997).

Figure 2-2a: Temperature profile, evolution of silica primary particle diameter, $d_p$, as predicted by using the characteristic sintering time, $\tau_{s,X}$, and $\tau_{s,X}$ for total inlet gas flowrate, $Q_o$, of 5550 cm$^3$/min and precursor (HMDSO) initial concentration of $5.93 \times 10^{-5}$ mol/g$_{\text{gas}}$.

Figure 2-2b shows the evolution of silica primary particle diameter from the burner of Briesen et al. (1998) as calculated by Equations 2-1 - 2-3 and the proposed sintering time, $\tau_s$ (Equation 2-14) for the same conditions as in Figure 2-2a. It is remarkable that the primary particle diameter reaches its final size (15 nm) only within the first centimeter from the burner outlet. Above this size, $\tau_s$ increases sharply (broken line) so sintering becomes extremely slow further obstructing primary particle growth.
Figure 2-2b: Evolution of silica primary particle diameter, \( d_p \), as predicted by using the proposed sintering time, \( \tau_s \), along with the evolution of \( \tau_c \) and the characteristic coagulation time, \( \tau_c \), for the same conditions as in Figure 2-2a. At the very early stages of particle growth the proposed sintering rate is much faster than that of Xiong et al. (1993).

The proposed sintering time, \( \tau_s \), is much more sensitive to small primary particle sizes than \( \tau_{s,X} \). More specifically, \( \tau_s \) is always lower than that of Xiong et al. (1993). The gap between \( \tau_s \) and \( \tau_{s,X} \) narrows down as primary particle size increases and temperature drops. At the early stages of particle growth (Figure 2-2b: \( d_p < 2 \) nm), despite the relatively low temperatures (500 K < \( T < 1000 \) K), the proposed sintering time has a low finite value (approximately in the order of \( 10^{-4} \) s) while \( \tau_{s,X} \) is extremely high. Both sintering times decrease following the temperature increase which at this stage (\( x < 0.2 \) cm) has a more dominant effect on sintering than particle size. This effect however is more pronounced for \( \tau_{s,X} \) which decreases at a much faster rate than \( \tau_s \). It is also worth noting that \( \tau_{s,X} \) reaches
a minimum at the peak of the temperature profile (Figure 2-2a) while $\tau_s$ starts increasing earlier at lower temperatures. Thereafter, for $d_p \approx 15$ nm (or $d_p \approx 0.7$ nm in Figure 2-2a), as temperature drops ($x > 0.5$ cm), both $\tau_s$ and $\tau_{s,X}$ steeply increase.

It should be mentioned here that the differences observed between the sintering time by Ehrman et al. (1998) and that by Xiong et al. (1993) were minimal. In conclusion, Figure 2-2b demonstrates the higher sensitivity of the proposed sintering rate on small particle sizes in contrast to Xiong et al. (1993) and Ehrman et al. (1998), but consistent with Rogak (1997) and Xing and Rosner (1999). Figure 2-2b also shows the evolution of the characteristic coagulation time, $\tau_c = 2/(\beta N \cdot \rho_g)$ (Friedlander, 1977). When $\tau_s > \tau_c$, aggregates that do not fully coalesce are formed (Lehtinen et al., 1996).

Figure 2-3 depicts the evolution of the number of primary particles per aggregate, $n_p$, as predicted by the use of $\tau_{s,X}$ (bold lines) and $\tau_s$ (thin lines) for the same temperature profile and inlet conditions as in Figure 2-2a, in the absence (solid lines) or presence (broken lines) of chemical reaction (Equation 2-18). Initially, $n_p$ increases up to 840 (at $x \approx 0.02$ cm) and then drops below 10 at a distance of approximately 0.35 cm from the burner face (Figure 2-3; thin solid line) when using $\tau_s$ and neglecting the reaction of HMDSO. The initial increase of $n_p$ is attributed to the high collision rates among small particles (for $d_p$ slightly above $d_{p,min}$) of high mobility. Indeed, very close to the burner face ($x < 0.02$ cm) the characteristic time for coagulation is smaller than that for sintering (Figure 2-2b). This means that small primary particles collide with each other much faster than the time needed for the complete fusion of the forming aggregates.

This will go on till the two competing mechanisms of coagulation and sintering become of the same order of magnitude (approximately at $5 \times 10^{-4}$ s or at $x \approx 0.02$ cm). Up to that point the SiO$_2$ primary particle diameter has increased only by a factor of $\sim 4$ (Figure 2-2b) from the initial molecular size (0.44 nm). After that, as temperature increases (Figure 2-2a) and the number concentration and size of aggregate particles further decrease, the coagulation time gradually increases and even becomes larger than the sintering time. Meanwhile, the number of primary particles per aggregate is steadily decreasing to reach a
minimum \( (n_p = 8) \) at around 0.45 cm from the burner (Figure 2-3; thin solid line). It is at this point where the primary particle diameter has already reached almost 90% of its final value that coagulation starts to outperform sintering again. The above described evolution of primary particle number, \( n_p \), is different from the one observed by Kruis et al. (1993) for silicon particles. In that case there is a monotonic increase of \( n_p \) with residence time mainly stemming from the initially smaller sintering than coagulation rate.

Figure 2-3: Evolution of the number of primary particles per aggregate, \( n_p \), for the same conditions as in Figure 2-2a, in the presence (broken lines) and absence (solid lines) of HMDSO reaction for the proposed sintering time (Equation 2-14; thin lines) and the sintering time by Xiong et al. (1993) (Equation 2-6; bold lines).

When the reaction rate of HMDSO is accounted for (Appendix A), the final primary particle size decreases by less than 12% following the slight delay in the particle number concentration build-up (i.e. for the conditions of Figure 2-2b the final primary particle diameter is 15 nm or 13.6 nm when neglecting or accounting for the chemical reaction,
respectively). The evolution of \( n_p \) with the effect of HMDSO decomposition (thin broken line) does not exhibit an initial local maximum at \( n_p = 840 \) but at \( n_p = 2 \) as the initial characteristic time for coagulation is now bigger than that for sintering. The steep increase of \( n_p \) from 1 to 2 (at approximately 1 mm from the burner face) stems from the fast completion of the reaction at this point. In addition, the final aggregate size (at a distance of 15 cm from the burner face) corresponds to approximately 230 primary particles. This value is larger than the one observed when the precursor decomposition is neglected (at \( x = 15 \) cm, \( n_p = 180 \)) basically resulting from higher aggregate collision rates following the completion of the reaction. This is also why the rate of increase of \( n_p \) is higher when accounting for the reaction. Similar results are derived when the sintering time by Xiong et al. (1993) is used (bold lines). The basic difference though is that when considering the effect of HMDSO decomposition (bold broken line), \( n_p \) rises faster (in comparison with the thin broken line) following the steep rise of \( \tau_{s,x} \) (Figure 2-2a).

The present model was also used for the simulation of several other experimental data by Briesen et al., (1998). Figure 2-4 shows a comparison between simulation and experimental results for the flame synthesis of \( \text{SiO}_2 \) by HMDSO decomposition for the conditions stated in Table 2-1 (Briesen et al., 1998). The model predictions based on the proposed sintering time (Equation 2-14) are in good agreement with experimental measurements of primary particle diameters measured by BET analysis. Using the sintering time by Xiong et al. (1993) predicts primary particle diameters that follow the trend of the experimental data, but it steadily underpredicts them by at least an order of magnitude. Similar results to the ones estimated when using the sintering rate by Xiong et al. (1993) are derived when the characteristic sintering time by Ehrman et al. (1998) is also tested. Furthermore, when this sintering time is corrected following Equation 2-13, the differences between simulation results and predictions by Equation 2-14 are only marginal.

Figure 2-5 depicts similar comparisons for \( \text{SiO}_2 \) synthesis by \( \text{SiCl}_4 \) reaction for the conditions listed in Table 2-1 (Briesen et al., 1998). Fast depletion of the precursor is assumed as hydrolysis of \( \text{SiCl}_4 \) (by water produced by the combustion of methane) occurs readily even at room temperature (Bautista and Atkins, 1991). Again, the agreement
between experiments and simulation results derived from the proposed sintering model (Equation 2-14) is good. Moreover, when compared to the predictions of the available sintering rate by Xiong et al. (1993) (or even by Ehrman et al., 1998), the present model still yields better agreement with data. In general, the predicted primary particle diameters by $\tau_s$ are higher than those by $\tau_{s,X}$, by almost a factor of 10. Finally, the proposed sintering model agrees fairly well even with the experimental data of Ehrman et al. (1998) for HMDSO (Figure 2-4) or SiCl$_4$ (Figure 2-5). More specifically, the predicted primary particle diameter is 8.5 nm which is in reasonably good agreement with the measured value of 10 nm by TEM analysis (square symbol in Figures 2-4 and 2-5)

![Diagram](attachment:image.png)

*Figure 2-4: Comparison of experimental primary particle size of silica from HMDSO (Briesen et al., 1998; Ehrman et al., 1998) with model predictions using the sintering time by Xiong et al. (1993) and the proposed one (Equations 2-6 and 2-14, respectively).*
Figure 2-5: Comparison of experimental primary particle size of silica from SiCl₄ (Briesen et al., 1998; Ehrman et al., 1998) with model predictions using the sintering time by Xiong et al. (1993) and the proposed one (Equations 2-6 and 2-14, respectively).

Seto et al. (1997) studied the sintering process of already formed silica aggregates with an average mobility (or surface area equivalent) diameter of 66 nm and an average primary particle size of 9.4 nm. They predicted well their experimental results (Figure 2-6; bold solid lines) using \( \tau_{s,x} \) and a two dimensional volume-area population balance model accounting for the complete size distribution. The present model and more specifically Equation 2-3 (since only sintering is considered here) is applied on the experimental conditions of Seto et al. (1997). Figure 2-6 also shows the predictions of this simple monodisperse model using \( \tau_s \) (thin solid lines) and \( \tau_{s,x} \) (thin broken lines). The agreement with experimental measurements is good for furnace process temperatures up to 1773 K. However, at larger temperatures the present sintering model \( \tau_s \) (Equation 2-14) overpredicts the experimental values of primary particle diameters. Consequently, the
Figure 2-6: Average mobility diameter (open circles) and primary particle diameter (filled circles) for silica aggregates as a function of furnace hot-wall temperature (Seto et al., 1997). Comparison of experimental data (symbols) with model predictions (lines) using the sintering time by Xiong et al. (1993) and the proposed one (Equations 2-6 and 2-14, respectively). The predictions of the polydisperse model of Seto et al. (1997) are also shown.

Aggregate mobility diameters are underpredicted. Similar trends are observed when $\tau_{s,X}$ (Xiong et al., 1993) is used, with the exception that the above mentioned differences occur at higher temperatures (> 1900 K). Both sintering models predict full sintering of the initial aggregates at a size of approximately 35 nm while the experimental data indicate that higher temperatures are needed for the aggregates to be completely coalesced. It should be noted that the initial aggregate sizes in Seto et al. (1997) are lognormally distributed and not monodisperse. Thus, the difference between the present monodisperse model simulations and the polydisperse model of Seto et al. (1997), may arise from the assumption of the monodispersity of the aggregate size for the calculation of the initial aggregate surface area.
which is needed for the solution of Equation 2-3. This can be improved by detailed but efficient population balance simulations of primary and aggregate particle dynamics (Tsantilis and Pratsinis, 2000).

2.4. CONCLUSIONS

A new characteristic sintering time for silica nanoparticles which sinter by a viscous flow mechanism, is introduced. The proposed sintering time is based on the particle size dependence of the melting point and predicts faster sintering rates at small particle sizes than existing sintering models relying solely on bulk material properties. It also determines a minimal stable primary particle size $d_{p,\text{min}}$ below which sintering is virtually instantaneous. The selected value of $d_{p,\text{min}} = 1$ nm is consistent with molecular dynamics studies.

The new characteristic sintering time provides a way of accounting for the behavior of nanosized particles during the initial stages of their formation and growth and results in good agreement between model predictions and experimental data for gas phase formation of silica particles by fast reaction of hexamethyl-disiloxane (HMDSO) and silicon-tetrachloride ($\text{SiCl}_4$) in premixed flames. Under the same conditions, the predictions of existing sintering time models were poor. The employed $d_{p,\text{min}}$ should be considered as an approximation to the actual value. For a detailed determination a larger set of data has to be evaluated and additional molecular dynamics as well as population balance calculations need to be carried out.

2.5. NOTATION

$C_{\text{HMDSO}}$   HMDSO concentration, mols/g<sub>gas</sub>
$D_f$           mass fractal dimension
$d_c$           collision diameter of aggregate, cm
$d_p$           primary particle diameter, cm
$d_{p,\text{min}}$   minimum primary particle diameter, $(4/(L\cdot\rho_s))(\sigma_s - \sigma_i(\rho_s/\rho_i)^{2/3})$, cm
\( E \) reaction activation energy, J/mol
\( E_{\text{bulk}} \) viscosity activation energy for the bulk material, J/mol
\( E_{\text{particle}} \) viscosity activation energy for the particle material, J/mol

HMDSO hexamethyldisiloxane \((\text{CH}_3)_6\text{Si}_2\text{O}\)

\( L \) latent heat of fusion, erg·g\(^{-1}\)

\( N \) number concentration of aggregates, aggregates/g\(_{\text{gas}}\)
\( N_o \) initial concentration of silica molecules, molecules/g\(_{\text{gas}}\)

\( n_p \) number of primary particles per aggregate

\( Q_o \) gas reference flowrate, cm\(^3\)/min

\( R \) universal gas constant, J/(mol·K)

\( S \) cross sectional area of flow, cm\(^2\)

\( s_c \) parameter for temperature profile (Equation 2-16), cm
\( s_h \) parameter for temperature profile (Equation 2-16), cm

\( T^* \) parameter for temperature profile (Equation 2-16), K

\( T_a \) adiabatic flame temperature in the absence of precursor, K

\( T_{a,H} \) adiabatic flame temperature in the presence of HMDSO, K

\( T_{a,S} \) adiabatic flame temperature in the presence of SiCl\(_4\), K

\( T_{m,\text{bulk}} \) melting point for the bulk material, K

\( T_{m,\text{particle}} \) melting point for the particle material, K

\( T_o \) gas reference temperature, K

\( T(x) \) temperature profile, K

\( u_x \) average velocity, cm/s

\( v \) volume of aggregate particle, cm\(^3\)

\( v_o \) equivalent-sphere volume of a silica molecule, cm\(^3\)

\( v_p \) primary particle volume, cm\(^3\)

Greek letters
\( \alpha \) area of aggregate particle, cm\(^2\)
\( \alpha_o \) equivalent-sphere surface area of a silica molecule, cm\(^2\)

\( \alpha_s \) area of a spherical aggregate, cm\(^2\)

\( \beta \) collision kernel between aggregates, cm\(^3\)/s

\( \mu \) viscosity, g·cm\(^{-1}\)·s\(^{-1}\)

\( \rho_g \) gas density, g/cm\(^3\)

\( \rho_l \) liquid density, g/cm\(^3\)

\( \rho_p \) SiO\(_2\) particle density, g/cm\(^3\)

\( \rho_s \) solid density, g/cm\(^3\)

\( \sigma_l \) liquid-gas surface tension, erg·cm\(^{-2}\)

\( \sigma_s \) solid-gas surface tension, erg·cm\(^{-2}\)

\( \tau_{s,E} \) characteristic sintering time for aggregates (Equation 2-7), s

\( \tau_{s,X} \) characteristic sintering time for aggregates (Equation 2-6), s

\( \tau_s \) characteristic sintering time for aggregates (Equation 2-14), s

\( \tau_c \) characteristic collision time for aggregates, s

2.6. REFERENCES


3. POPULATION BALANCE MODELING OF FLAME SYNTHESIS OF TITANIA NANOPARTICLES

ABSTRACT

The significance of various particle formation pathways during flame synthesis of titania nanoparticles by titanium tetraisopropoxide (TTIP) decomposition in a premixed methane-oxygen flame is investigated by population balance modeling. An efficient moving sectional model is developed accounting for gas phase chemical reactions, coagulation, surface growth and sintering assuming monodisperse primary particle size distribution in each volume section. The model is validated by comparing it against standard sectional solutions and detailed but cumbersome literature models at certain limiting cases (i.e., only coagulation and sintering, only surface growth or only coagulation). The evolution of primary particle size distribution is monitored by rapid thermophoretic sampling and image analysis of transmission electron microscope (TEM) pictures while the corresponding flame temperature is measured in the presence of particles by Fourier transform infrared spectroscopy. Excellent agreement is obtained between model predictions and data with respect to the evolution of average primary particle diameter and geometric standard deviation without any adjustable parameters until conditions of pure agglomeration of polydisperse particles are established (here, approximately after the first 9 cm above the burner tip). By comparing detailed measured and calculated size distributions, surface reaction appears to be the dominant route for early particle growth at the conditions studied.

3.1. INTRODUCTION

Flame processes are by far the most widely used ones for manufacture of commercially available quantities of nanoparticles (such as carbon blacks, fumed silica and pigmentary titania). Typically, in flame reactors, nanostructured powders are produced virtually without control at high temperatures and extremely short process residence times (usually, less than a second). This makes representative particle sampling, model development and process control quite challenging (Pratsinis, 1998). As a result, there is a
great interest to better understand the basic phenomena by detailed theoretical and experimental studies so as to optimally design flame reactors by interfacing fluid and particle dynamics (Johannessen et al., 2000)

Ulrich and Riehl (1982) monitored the evolution of flame-made silica particles by laser scattering. Even though they simulated well particle dynamics by a population balance model that involved an arbitrary shape factor, they were not able to distinguish between aggregate and primary particle sizes. Zachariah and Semerjian (1989) found good agreement with experimental results at high precursor concentrations during the formation of silica particles from silane in an opposed jet reactor but did not distinguish between aggregate and primary particle sizes or gas and surface reactions. Hung and Katz (1992) combined dynamic light scattering and thermophoretic sampling techniques to determine the effect of process conditions, such as temperature and precursor concentration, on the formation of TiO$_2$-SiO$_2$ mixed powders in an oxy/hydrogen counterflow diffusion flame reactor. Lee et al. (2001) simulated aggregate particle growth in this reactor by considering the effect of axial particle diffusion and using a two dimensional sectional model (Xiong and Pratsinis, 1993) for coagulation and sintering along with multi-step hydrogen/oxygen reactions (including both oxidation and hydrolysis of SiCl$_4$) and flame temperature measurements in the absence of particles. Lindackers et al. (1997) used a particle mass spectrometer (PMS) to monitor the growth of SiO$_2$ particles in a premixed low pressure H$_2$/O$_2$/Ar flame doped with SiH$_4$. A theoretical model including, full homogeneous H$_2$/O$_2$ and SiH$_4$/O$_2$ kinetics, estimated temperatures by a flame model (PREMIX) and sectional calculations for SiO$_2$ homogeneous nucleation and Brownian coagulation, was in good agreement with experimental data. Tsantilis and Pratsinis (2000) described the evolution of both aggregate and primary particle size distributions by incorporating the effect of sintering and mass fractal dimension in the sectional model of Hounslow et al. (1988) and achieved good agreement with the experimental aggregate size distributions of Akhtar et al. (1991). Recently, Jeong and Choi (2001) used a single surface fractal dimension to correlate particle volume and area in a given size interval and thus simplified the detailed two-dimensional sectional model of Xiong and Pratsinis (1993) for coagulation and sintering into a set of two one-dimensional sectional equations for particle volume and area,
respectively. In addition, they stated that the above modification could decrease computation time by approximately three orders of magnitude without seriously diminishing the accuracy of their calculations.

Of particular interest is the investigation of the competition between gas phase and surface reaction mechanisms as these could be quite critical for explaining the dominant trends of particle formation and growth (i.e., surface growth dominates carbon black production while gas phase reaction dominates the production of fumed silica). Pratsinis and Spicer (1998) studied the effect of TiCl$_4$ surface reaction (that is oxidation of TiCl$_4$ on the surface of TiO$_2$ spherical particles) on the size of product titania (TiO$_2$) particles over a wide range of process conditions. They developed a monodisperse model and showed that TiCl$_4$ surface oxidation is more important (compared to gas phase oxidation) at high TiCl$_4$ initial concentrations.

![Diagram](image)

**Figure 3-1a.** Schematic of the physico-chemical processes contributing to the synthesis of titania nanoparticles by TTIP in a premixed flame. TTIP molecules (gray spheres) decompose (in the gas phase) to produce TiO$_2$ monomers (molecules) which later grow to bigger particles (black spheres) by coagulation. TTIP molecules can also decompose on the surface of TiO$_2$ particles thus increasing aerosol volume while particles can acquire irregular shapes due to slow sintering.
In retrospect, there are few studies describing the detailed evolution of aggregate and primary particle characteristics in flames (Figure 3-1a). More specifically, the early stage of particle formation is one of the areas that is ripe for better understanding as instruments that allow for accurate non-intrusive measurements are now available. Fourier Transform Infra-Red (FTIR) spectroscopy is for instance particularly attractive as it concurrently provides information on the flame temperature, gas composition and particle concentration during flame synthesis (Farquharson et al., 1998; Morrison Jr. et al., 1997; Best et al., 1986). Likewise, particle sizing at different locations along the flame can be made accurately by thermophoretic sampling (TS) followed by computer image analysis of transmission electron micro-graphs (Dobbins and Megaridis, 1987). The insertion of the TEM grid is practically instantaneous, causing minimal disturbance to the upstream motion of the flame gases and particle history (Arabi-Katbi et al., 2001).

The present paper relies on those techniques to provide an insight on the full evolution of primary particle size distribution. This provides the opportunity to overcome the limitations of past studies (Okuyama et al., 1986; Xiong et al., 1993; Briesen et al., 1998; Johannessen et al., 2000) which typically relied on particle data collected after the process was complete. Therefore, such an investigation could reveal, for instance, the importance of surface growth or other reaction routes, especially at the early stages of particle formation and growth. It should be noted that such an investigation is difficult to carry out by merely analyzing collected powder samples far away from the particle source since for most aerosol processes, coagulation usually obscures the initial steps of particle evolution, leading (given sufficient residence time, typically in the order of 1 s) to the attainment of an asymptotic value (the so-called self preserving particle size distribution) irrespective of the initial growth mechanisms.

More specifically, the fundamental processes contributing to the observed evolution of titania particle size distribution are investigated by developing a sectional model that describes particle formation by gas phase and surface growth reactions followed by coagulation and sintering (Figure 3-1a), therefore covering the whole spectrum of particle evolution till the final collection point, typically governed by coagulation and small sintering rates. The significance of gas phase chemical reactions (Okuyama et al., 1990;
Kashima and Sugiyama, 1990; Seto et al., 1995) and surface growth (Battiston et al., 1997, 1999) of titanium tetraisopropoxide (TTIP) on product TiO$_2$ particle size is examined by comparisons between experimental data and model predictions of the evolution of primary particle size distributions along the flame.

### 3.2. EXPERIMENTAL

Titania particles are made from TTIP in a premixed methane-oxygen flat flame (Arabi-Katbi et al., 2001). Figure 3-1b shows the experimental set-up with the premixed flame aerosol reactor, the thermophoretic sampler and the Fourier transform infra-red (FTIR) spectrometer. The flame reactor consists of three concentric quartz glass tubes. The premixed reactants though are fed through the middle (central) tube with a 25 mm diameter. The flow rates of methane, oxygen and nitrogen are 0.4, 1.2, and 3.95 L/min, respectively. TTIP is added by saturating 0.65 L/min argon in a temperature controlled washing bottle containing liquid TTIP, resulting in a production rate of 3.1 g/h TiO$_2$ (corresponding to a precursor mass flow rate of approximately 11 g/h). The flame is stabilized on a 38 mm long mullite honeycomb (64 openings/cm$^2$). All the gases and the manifold are heated 20 K above the liquid TTIP temperature, to prevent condensation. Powders are collected on glass fiber filters, kept 20 cm above the burner tip.

The FTIR (Bomem Inc., Model MB157) operates over the spectral range 6500-500 cm$^{-1}$ (1.5 - 20 µm) with a resolution of 2 cm$^{-1}$ and paraboloidal mirrors that focus the IR-beam (4mm in diameter) through the flame (Figure 3-1b). Temperatures are estimated from emission (radiance) and transmission measurements, using the so-called ET (Emission-Transmission) and Normrad (Normalized-Radiance) procedures (Morrison et al., 1997; Arabi-Katbi et al., 2001). As the flame is not truly optically thin, the emission (radiance) is corrected for self-absorption (Freeman and Katz, 1960) following Best et al. (1991). In both evaluation methods emphasis is put on the CO$_2$ peaks at 2350 cm$^{-1}$ (as they are the clearest in the spectrum) and the CO$_2$ concentration (Arabi-Katbi et al., 2001). For every location along the flame, the average temperature is obtained with ET and Normrad procedures, which usually exhibit a difference of less than 50 K. Temperature integral measurements
are performed along the symmetry axis (r = 0 cm). For completeness, it should be noted here that the accuracy of the FTIR temperature measurements has already been verified by comparing FTIR, coherent anti-Stokes Raman spectroscopy (CARS) and thermocouple measurements in diffusion (Best et al., 1991) and premixed (Kammler et al., 2002) flames.

Figure 3-1b. Schematic of the experimental set-up used for synthesis of titania nanoparticles by TTIP in a premixed methane-oxygen flat flame (only the inner tube of the depicted burner is used to carry the reacting gases). A Fourier Transform Infra-Red (FTIR) spectrometer, for temperature measurements, and a pneumatic Thermophoretic Sampler (TS), for collection and image analysis of particles, are also shown.

Thermophoretic sampling is performed using a system similar to that invented by Megaridis (Dobbins and Megaridis, 1987; Megaridis, 1987) and is the same as the one described in detail by Arabi-Katbi et al. (2001). After the sampling, TEM-micrographs (Figure 3-2a) are obtained with a Hitachi 600 transmission electron microscope operating at 100 kV (magnifications of 20-30k). At each location, more than 1000 particles (sampled on
different grids) are counted using the software Optimas 6.51 (Media Cybernetics L. P.) for the derivation of particle statistics (including for instance, average primary particle sizes and size distributions as well as the corresponding standard and geometric standard deviations, $\sigma$ (nm) and $\sigma_{g,p}$, respectively). The image analysis of the TEM pictures of grids collected at different (centerline) locations above the burner tip is shown in Figure 3-2b depicting the effect of the number of counts on the calculation of the Sauter mean, $d_{ps}$ (Hinds, 1999), primary particle diameter and the (number based) geometric standard deviation, $\sigma_{g,p}$ (Hinds, 1999), of the primary particle size distribution. For all the collection points along the flame ($x = 0.5, 0.8, 1.3, 2.3, 4.0$ and $5.5$ cm), counting more than 300 particles changes the estimated Sauter mean diameter and the geometric standard deviation by less than 7 % and 3 %, respectively. A complete set of TEM pictures collected from different locations of the present premixed flame configuration (Figure 3-1b), for $11$ g/h of TTIP is shown in Kammler et al. (2001).

![Figure 3-2a. Transmission Electron Microscope (TEM) picture of titania nanoparticles collected with the thermophoretic sampler at 4.0 cm above the burner tip. At this location particles are spherical with virtually no degree of aggregation or neck formation. Similar transmission electron micrographs are taken from different locations along the flame. For each location more than 1000 primary particles are counted.](image)
Figure 3-2b. Effect of the number of counts on the estimation of the Sauter mean primary particle diameter (squares), and the (number based) geometric standard deviation of the primary particle size distribution (triangles), from the image analysis of TEM pictures of grids collected at different (centerline) locations above the burner tip.
Finally, the specific surface area of the powder collected on the glass fiber filter (Gelman, 142 mm diameter) is measured by nitrogen adsorption (Gemini 2350, Micromeritics) at 77 K with a five point isotherm in the relative pressure range of 0.05-0.25, following the BET-theory. Before adsorption, the samples are degassed (Flow prep 060, Micromeritics) under nitrogen atmosphere at 150°C for two hours. It should be noted that particle collection on the filter (at 20 cm from the burner tip) is necessary since the low temperatures (~300 K) prevailing far away from the flame render thermophoretic sampling ineffective.

3.3. THEORY

3.3.1. Reaction Models

The depletion of TTIP occurs by both homogeneous gas phase reaction and by reaction at the surface of existing TiO$_2$ particles (Pratsinis and Spicer, 1998):

$$\frac{dC}{dt} = -kC = -(k_g + k_s A \rho_g)C$$

where $C$ (molecules/g) is the concentration of TTIP, $t$ (s) is the residence time, $A$ (cm$^2$/g) is the total surface area concentration of TiO$_2$ particles, $\rho_g$ (g/cm$^3$) is the carrier gas density (based on air), $k$ (1/s) is the overall reaction rate constant, $k_g$ (1/s) is the gas phase reaction rate constant and $k_s$ (cm/s) is the surface reaction rate constant of TTIP. Based on the literature of titania synthesis by TTIP, three possible chemical pathways are investigated:

(A) gas phase thermal decomposition of TTIP (Okuyama et al., 1990):

$$\text{TTIP}_{(\text{gas})} \rightarrow^{k_g} \text{TiO}_2 + 4\cdot\text{C}_3\text{H}_6 + 2\cdot\text{H}_2\text{O}$$

as the sole source of titania molecules, where $k = k_g = (3.96 \times 10^5 \exp(-8479.7/T))$, and $T$ (K) is the gas temperature.

(B) gas phase hydrolysis of TTIP (Seto et al., 1995):

$$\text{TTIP}_{(\text{gas})} + 2\cdot\text{H}_2\text{O} \rightarrow^{k_s} \text{TiO}_2 + 4\cdot\text{C}_3\text{H}_7\text{OH}$$

as the sole source of titania molecules where $k = k_g = (3 \times 10^{15} \exp(-1013.9/T))$. Water comes mainly from combustion of CH$_4$ and to a lesser extend from the decomposition of TTIP.

(C) gas phase and surface thermal decomposition of TTIP:
\[
TTIP_{(\text{gas})} \xrightarrow{k_g} TiO_2 + 4\cdot C_3 H_6 + 2\cdot H_2 O \quad (3-4)
\]

\[
TTIP_{(\text{particle surface})} \xrightarrow{k_s} TiO_2 + \ldots \quad (3-5)
\]

where \( k = k_g + k_s \cdot A \cdot \rho_g \). The thermal decomposition of TTIP is now considered as an overall reaction since its measurement included synthesis of titania particles (Okuyama et al., 1990). Although there is a large scattering of data in the open literature regarding surface growth kinetics of titania, they strongly depend on the experimental conditions such as pressure, process temperature and carrier gas composition (Siefering and Griffin, 1990; Kamata et al., 1990) under which they were originally estimated. However, Battiston et al. (1997, 1999) distinguished between surface and parasitic homogeneous reactions and proposed a first order (with respect to TTIP) surface reaction during synthesis of TiO\(_2\) thin films that, in contrast to previous studies, was not dependent on the presence or absence of oxygen. Thus here, in lack of other suitable data, the surface reaction constant is approximated using the reaction model and experimental data of Battiston et al. (1997; Equation 7 and Figure 9, respectively) to derive: \( k_s \approx 1 \times 10^{11} \exp(-15155.16/T) \) cm/s. Furthermore, the gas phase reaction constant is calculated by: \( k_g = k - A \cdot k_s \cdot \rho_g \). The above surface reaction rate \( (k_s) \) should be treated with caution, as the data of Battiston et al. (1997, 1999) were obtained in the temperature range of 660 K to 700 K which is lower than the one considered in the simulations of the present study. Indeed, such low temperature conditions are typically encountered in titania thin film metal-organic chemical vapor deposition (MOCVD) to minimize "parasitic" reactions and particle nucleation that could contaminate the growing surface with unwanted particles. Nevertheless, both the first and second Damköhler numbers (Brodker and Hershey, 1988), under the conditions of the present study and the surface reaction rate from Battiston et al. (1997, 1999), are much smaller than 1, thus indicating that there are no mass transfer limitations in surface growth that could directly render the applied surface reaction kinetic model invalid (Appendix B).

A combination of cases (B) and (C) is not included here, as the present reaction rate of hydrolysis is so fast (virtually instantaneous for the temperature profiles of the present study) that gas and surface thermal decomposition reactions become practically ineffective. Finally, at high precursor concentrations, the rate of TTIP consumption by surface reaction...
employed here may exceed the overall rate predicted by Okuyama et al. (1990). When this is the case, the surface reaction rate is taken as \( k_s = k / (A \cdot \rho_g) \) and \( k_g \) is set equal to zero so that the mass balance is preserved.

### 3.3.2. Moving Sectional Aerosol Dynamics Model

As demonstrated in earlier studies (Hounslow et al., 1988; Kumar and Ramkrishna 1996a, b; 1997; Tsantilis and Pratsinis, 2000; Jeong and Choi 2001), the considerable increase of computational power, along with the development of efficient models render sectional calculations an increasingly attractive simulation tool providing accurate and detailed information on the dynamics of particle size distributions. Here, the proposed sectional formulation accounts for simultaneous gas phase chemical reaction (or nucleation), surface growth, coagulation and sintering and constitutes an extension of the moving sectional model of Kumar and Ramkrishna (1997) to include a new discretization for nucleation by Chaoul (2000) and Spicer et al. (2002) as well as sintering and particle shape irregularity effects following the approach of Vemury et al. (1994). The latter used the sectional model of Batterham et al. (1981) and proposed a sectional equation for the change in particle surface area concentration, \( A_i \), by pure agglomeration (particle collisions without coalescence), by substituting the particle volume concentration in each size interval \( i \) with the corresponding particle surface area concentration. The total change of \( A_i \) by coagulation and sintering was then given as:

\[
\frac{dA_i}{dt} = \frac{dA_i}{dt}_{agg} + \frac{dA_i}{dt}_{sint}
\]  

(3-6)

However, since the model of Batterham et al. (1981) contains systematic inaccuracies in the preservation of both total particle mass and numbers (Hounslow et al., 1988), the moving sectional formulation of Kumar and Ramkrishna (1997) is more appropriate, especially when dealing with surface growth reaction modes that can produce (in the absence of a moving sectional technique) significant numerical diffusion errors.

Therefore, the evolution (by coagulation) of the particle number concentration \( N_i \) (particles/g), in a given section \( i \), is (Kumar and Ramkrishna, 1996a, 1997):
\[
\frac{dN_i}{dt}_{agg} = \sum_{i \leq j \leq k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k \left( \frac{x_{i-1} - v}{x_{i-1} - x_i} \right) \rho_g \\
+ \sum_{x_i, x_j, x_k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k \left( \frac{x_{i+1} - v}{x_{i+1} - x_i} \right) \rho_g - N_i \sum_{k=1}^M \beta_{i,k} N_k \rho_g \quad (3-7)
\]

where \( M \) is the total number of sections (bins), \( \delta_{j,k} \) is the so-called Dirac delta function (equal to 1 for \( j = k \), and equal to 0 for \( j \neq k \)), \( x_i \) (cm\(^3\)) is the pivot volume in section \( i \) with boundaries \( v_i \) and \( v_{i+1} \), \( v = x_j + x_k \) and \( \beta_{j,k} \) (cm\(^3\)/s) is the Brownian collision frequency function between particles in pivots \( j \) and \( k \), spanning over the free-molecular, transition, and continuum regimes (Fuchs, 1964; Seinfeld, 1986). Equation 3-7 is a simplification of the general equation shown in Kumar and Ramkrishna (1996a, 1997), representing here the case of preservation of mass and numbers. Multiplying both sides of Equation 3-7 with \( x_i \):

\[
\frac{dN_i}{dt}_{agg} = \sum_{i \leq j \leq k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k x_i \left( \frac{x_{i-1} - v}{x_{i-1} - x_i} \right) \rho_g \\
+ \sum_{x_i, x_j, x_k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k x_i \left( \frac{x_{i+1} - v}{x_{i+1} - x_i} \right) \rho_g - x_i N_i \sum_{k=1}^M \beta_{i,k} N_k \rho_g \quad (3-8)
\]

Extracting the ratio \( v/x_i \) from the volume fractions in the right hand side (RHS) results in:

\[
\frac{dV_i}{dt}_{agg} = \sum_{i \leq j \leq k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k x_i \left( \frac{x_{i-1} - 1}{x_{i-1} - x_i} \right) \rho_g \\
+ \sum_{x_i, x_j, x_k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} N_j N_k x_i \left( \frac{x_{i+1} - 1}{x_{i+1} - x_i} \right) \rho_g - V_i \sum_{k=1}^M \beta_{i,k} N_k \rho_g \quad (3-9)
\]

where \( V_i \) (cm\(^3\)/g) is the particle volume concentration in section \( i \). It should be noted here that in the above derivation the discretization for coagulation is fixed (Kumar and Ramkrishna, 1996a, 1997) and therefore \( x_i \) \((dN_i/dt) = (x_i) \) \( (N_i/dt) = (dV_i/dt) \). Using the definition of \( v = (x_j + x_k) \) and after some simple algebra, Equation 3-9 is further modified to:

\[
\frac{dV_i}{dt}_{agg} = \sum_{i \leq j \leq k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k} (N_j V_k + N_k V_j) \rho_g - V_i \sum_{k=1}^M \beta_{i,k} N_k \rho_g \quad (3-10)
\]
where now (for preservation of mass and numbers) the modified volume (interpolation) fractions become:

\[
\eta' = \begin{cases} 
\frac{x_{i+1}}{x_j + x_k} - 1 & x_i < x_j + x_k < x_{i+1} \\
\frac{x_{i+1} - 1}{x_i} & x_{i-1} < x_j + x_k < x_i \\
\frac{x_{i-1}}{x_j + x_k} - 1 & x_{i-1} < x_j + x_k < x_i \\
\frac{x_{i-1} - 1}{x_i} & x_i < x_j + x_k < x_{i+1} 
\end{cases}
\] (3-11)

Similarly to Vemury et al. (1994), volume and area are equivalent for pure agglomeration, thus replacing \( V_i \) with \( A_i \) in Equation 3-10 produces:

\[
\frac{dA_i}{dt}_{\text{agg}} = \sum_{j,k}^{i \times j < k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k}(N_j A_k + N_k A_j) \eta' \rho_g - A_i \sum_{k=1}^{M} \beta_{i,k} N_k \rho_g (3-12)
\]

The same approach can be followed to develop a sectional formulation for the evolution of area concentration by coagulation (and sintering) starting from the sectional model of Hounslow et al. (1988) (Appendix D). However, such a sectional formulation (based on Hounslow et al., 1988) is inherently confined to a fixed spacing factor, \( s = x_{i+1}/x_i = 2 \), and can not include surface growth due to numerical diffusion limitations.

When sintering, gas and surface chemical reactions are also considered, Equations 3-7 and 3-12 become:

\[
\frac{dN_i}{dt}_{\text{agg}} = k_g C_n_i \eta_i + \frac{dN_i}{dt}_{\text{agg}} \text{with } \eta_i = \begin{cases} 
1 & v_m \in [v_i, v_{i+1}] \\
0 & v_m \notin [v_i, v_{i+1}] 
\end{cases} (3-13)
\]

\[
\frac{dA_i}{dt} = k_g C_n_i \alpha_m + \sum_{j,k}^{i \times j < k} \left( 1 - \frac{1}{2} \delta_{j,k} \right) \beta_{j,k}(N_j A_k + N_k A_j) \eta' \rho_g - A_i \sum_{k=1}^{M} \beta_{i,k} N_k \rho_g - \frac{1}{\tau_{s,i}} (A_i - N_i \alpha_{i,s}) + 4\pi N_i n_{p,i} k_s d_{p,i} C_m \rho_g (3-14)
\]

where \( v_m \) (cm\(^3\)) is the volume of a TiO\(_2\) monomer equivalent sphere (~3.32\( \times \)10\(^{-23}\) cm\(^3\), corresponding to a volume equivalent diameter, \( d_m \), of approximately 0.4 nm), \( \alpha_m \) (cm\(^2\)) is
the corresponding TiO$_2$ monomer area, $\alpha_{i,s}$ (cm$^2$) is the area of a fully fused TiO$_2$ particle of volume $x_i$, $d_{p,i}$ (cm) = $(6N_i x_i)/A_i$ is the primary particle diameter in an aggregate of volume $x_i$ (Kruis et al., 1993; Tsantilis and Pratsinis, 2000), $n_{p,i} = A_i^3/(36\pi x_i^2 N_i^3)$ is the number of primary particles within that aggregate (Kruis et al., 1993; Tsantilis and Pratsinis, 2000) and

$$\tau_{s,i} (s) = 7.4 \times 10^8 \cdot T \cdot d_{p,i}^2 \cdot \exp(31000/T)$$

is the characteristic sintering time for titania (Kobata et al., 1991).

More specifically, the first RHS term in Equation 3-13 accounts for the birth of particles of monomer size by gas phase chemical reaction (thus, it is used only for $i = 1$) as titania particles in aerosol processes are typically formed in the absence of a nucleation barrier (Xiong and Pratsinis, 1991). Likewise, the first RHS term in Equation 3-14 accounts for the increase of particle area concentration by gas phase chemical reaction (nucleation), the second and third RHS terms account respectively for changes in aggregate area concentration by birth and death of particles in section $i$ by coagulation, the fourth RHS term accounts for the effect of sintering (Koch and Friedlander, 1990; Xiong and Pratsinis, 1993; Vemury et al., 1994; Pratsinis, 1998), while the last RHS term in Equation 3-14 represents the increase in aggregate area by surface growth (Appendix C). The derivation of Equations 3-13 and 3-14 further implies that surface growth and sintering have no effect on the aggregate particle number concentration. Moreover, the effect of aggregate structure on the coagulation rate, is considered by incorporating, in the collision frequency function $\beta_{j,k}$, the so called collision diameter (Kruis et al., 1993; Tsantilis and Pratsinis, 2000):

$$d_{c,i} = d_{p,i} \left( n_{p,i} \right)^{\frac{1}{D_f}}$$

(3-15)

where $D_f$ is the mass fractal dimension ranging from 1 to 3 (Kruis et al., 1993). Here, a typical value of 1.8 is used (Seto et al., 1997). This value is kept constant throughout the calculations as fractal dimensions may not be so sensitive to changes in simulation conditions such as sintering rates and process temperatures (Akhtar et al., 1994; Tsantilis and Pratsinis, 2000).

In order to avoid numerical diffusion when surface reactions take place, a moving sectional discretization for surface growth is also adopted (Kumar and Ramkrishna, 1997):
\[
\frac{dV_i}{dt} \bigg|_{\text{surf}} = N_i \frac{dx_i}{dt} \bigg|_{\text{surf}} = k_i CA_i v_m \rho_g \Rightarrow \frac{dx_i}{dt} \bigg|_{\text{surf}} = \frac{k_i CA_i v_m \rho_g}{N_i} = k_i Cn_{p_i} \pi d_{p_i}^2 v_m \rho_g (3-16)
\]

Although the technique, introduced by Kumar and Ramkrishna (1997), correctly accounts for the number of monomers (nuclei), it does not always represent the total mass of incoming nuclei correctly, as no equation for the effect of nucleation on the pivot of the first section is included. In general (as the pivot \(x_i=1\) moves away from \(v_m\) by surface growth), the total monomer mass can be considerably overpredicted (when nucleation and surface growth occur simultaneously) unless very short time steps are taken, in the expense of computation time. Therefore, a different approach is followed here for the effect of nucleation on the evolution of pivots, \(dx_i/dt\), that preserves both mass and numbers (Chaoul, 2000; Spicer et al., 2002):

\[
\frac{dx_i}{dt} = \frac{dx_i}{dt} \bigg|_{\text{nuc}} + \frac{dx_i}{dt} \bigg|_{\text{surf}} \quad \text{with} \quad \frac{dx_i}{dt} \bigg|_{\text{nuc}} = \frac{1}{N_i} (v_m - x_i) (k_g C) \eta_i (3-17)
\]

The system of differential equations to be solved for simultaneous nucleation, surface growth, coagulation and sintering includes Equations 3-13, 3-14 and 3-17 while the grid regeneration principles remain virtually the same as in Kumar and Ramkrishna (1997). In general, the goal is to regenerate the grid (preserving total mass, numbers and area) without decreasing the accuracy of the calculations and maintain a rather geometric resolution, as this guarantees low computational demands for a wide range of particle sizes; thus for instance, pivot \(x_i\) is eliminated when the ratio of the adjacent pivots \(x_{i+1}/x_{i-1}\) is smaller than a critical value \(r_{\text{critical}} = s^{1.1}\) (Chaoul, 2000). In addition, the initial spacing factor, \(s\), used in the present calculations is 2, while the number of sections ranged from 40 to 70.

Equations 3-13, 3-14 and 3-17 are further transformed into a spatial coordinate mode and readily integrated using the appropriate reaction rates for each case and the differential equation software DGEAR (IMSL, 1980). Typically, in a premixed flame configuration, radial temperature profiles are rather uniform (Arabi-Katbi et al., 2001) indicating a rather narrow residence time distribution (especially close to the burner tip), thus:
\[
\frac{dF}{dt} = \frac{dF}{dx} \frac{dx}{dt} = \frac{dF}{dx} u_x \quad (F = C, N_i, A_i, x_i)
\] (3-18)

where \(u_x\) (cm/s) is the gas average velocity which for the case of a premixed flat flame can be approximated as (Ehrman et al., 1998):

\[
u_x = \frac{Q_r}{S} \frac{T(x)}{T_r}
\] (3-19)

where \(S\) (cm\(^2\)) is the cross sectional area of the premixed burner, \(Q_r\) (cm\(^3\)/s) the total inlet gas volumetric flowrate (defined at 1 atm and \(T_r = 298\) K) and \(T(x)\) (K) is the axial temperature profile.

In the following sections, predictions of the sectional model will be discussed in terms of average diameters and geometric standard deviations. In order to assure consistent comparisons between predictions from a wide variety of methods, including sectional and monodisperse calculations as well as BET measurements and counts from TEM pictures, the average particle diameter used here is the Sauter mean primary particle diameter (Hinds, 1999):

\[
d_{ps} = \left( \frac{6 \sum_i N_i \cdot x_i}{\sum_i A_i} \right) = \left( \frac{\sum_i N_i \cdot n_{pi} \cdot d_{pi}^3}{\sum_i N_i \cdot n_{pi} \cdot d_{pi}^2} \right)
\] (3-20)

Finally, the geometric standard deviation (of the aggregates) is derived from Landgrebe and Pratsinis (1990; Equations B[4] and B[7]) using the density function (Kumar and Ramkrishna, 1997):

\[
n(v,t) = \sum_i N_i \cdot \delta(v - x_i)
\] (3-21)

and thus

\[
\ln^2 \sigma_g = \frac{1}{9} \int_0^{+\infty} n(v,t) \ln^2 \left( \frac{v}{v_g} \right) dv = \frac{1}{9} \sum_i \frac{N_i}{N} \ln^2 \left( \frac{x_i}{v_g} \right)
\] (3-22)

where

\[
N = \int_0^{+\infty} n(v,t)dv = \sum_i N_i \quad \text{and} \quad \ln v_g = \int_0^{+\infty} \frac{n(v,t)}{N} \ln vdv = \sum_i \frac{N_i}{N} \ln x_i
\] (3-23)
For the primary particles, the geometric volume, $v_{p,g}$, and geometric standard deviation, $\sigma_{g,p}$, are derived from equations 3-23 and 3-22 by replacing $N_i$ with $N_i n_{p,i}$, $N = \sum N_i$ with $\sum_i N_i n_{p,i}$, $v$ with $v_p$, and $x_i$ with $v_{p,i} = \pi d_{p,i}^3 / 6$.

### 3.4. RESULTS AND DISCUSSION

#### 3.4.1. Validation

The accuracy of the present (moving) sectional model (Equations 3-13, 3-14 and 3-17) is tested by a series of validation calculations. First, three different cases are considered that do not include surface growth (and consequently, also apply to the fixed sectional model shown in Appendix D). These are namely: pure agglomeration (coagulation of fractal like aggregate particles, consisting of primaries of monomer size), full coalescence (coagulation of spherical particles) and concurrent coagulation and sintering of fractal like aggregate particles. The first two cases are simulated, with the present (moving) sectional model, by merely setting the characteristic sintering time to the appropriate value (namely, $\tau_{s,i} \rightarrow \infty$ or practically $10^{10}$ s, for pure agglomeration and, $\tau_{s,i} \rightarrow 0$ or practically $10^{-10}$ s, for full coalescence) and $k_s = 0$. Comparisons with other (standard) models are carried out in terms of several aerosol population properties such as the total particle surface area and number concentrations, as well as the Sauter mean primary particle diameter and the diameter of average aggregate mass (Hinds, 1999). The predictions of the proposed moving sectional model reproduce the results of the model of Hounslow et al. (1988) or, equivalently, of Kumar and Ramkrishna (1996a) for a spacing factor of 2, in the absence or presence of a gas phase chemical reaction (i.e., thermal decomposition of TTIP). It should be noted that the original models of Hounslow et al. (1988) and Kumar and Ramkrishna (1996a) make no use of particle area concentrations, and therefore pure agglomeration and full coalescence in these formulations are directly simulated by respectively setting the collision diameter (Equation 3-15) equal to a function of monomer properties,
\[ d_{e,i} = d_{m} \left( \frac{\alpha_{m}^3}{36\pi v_{m}^2} \right)^{\frac{2}{3}} \text{, or to the volume equivalent diameter } d_{v,i} = \left( \frac{6\pi}{\pi} \right)^{\frac{2}{3}} \text{. The same results are also acquired with the fixed sectional model shown in Appendix D.} \]

Figure 3-3 shows the validation calculations (in terms of a) non-dimensional particle number concentration, \( N/N_0 \), b) average primary particle diameter and c) average number of primaries per aggregate) for instantaneous reaction, coagulation and sintering using the standard conditions of Kruis et al. (1993; Table 2) and four different sectional formulations, namely the present moving (solid lines) and fixed (Appendix D, open circles) sectional models, as well as the detailed two dimensional sectional model of Xiong and Pratsinis (1993) (squares) and the simple sectional model of Tsantilis and Pratsinis (2000) (diamonds). The results of the proposed moving and fixed sectional models are virtually identical both for 1073 K and 1273 K. In general, the agreement between the moving sectional model of this study and the detailed (but rigorous) two dimensional sectional model of Xiong and Pratsinis (1993) is fairly good. In contrast to the proposed sectional formulations, the model of Xiong and Pratsinis (1993) could accommodate more than one primary particle sizes within a given aggregate. Despite that, the agreement between the model of Xiong and Pratsinis (1993) and the two sectional models of this study is reasonably good even for the case of the average number of primaries per aggregate (Figure 3-3c), thus verifying the credibility (as far as integral properties are concerned) of the assumption of a single (but time dependent) primary particle diameter in every volume size interval (Vemury et al., 1994; Tsantilis and Pratsinis, 2000; Jeong and Choi, 2001). Furthermore, the predictions of the fixed sectional model (Appendix D) are better than those of Tsantilis and Pratsinis (2000), as in the latter case, the effect of coagulation on sintering is neglected.

Validation of the complete model for nucleation, surface growth, coagulation and sintering is not possible at this stage in lack of relevant analytical solutions or other standard numerical schemes. For completeness however, an additional validation test can be carried out regarding nucleation, coagulation (of spherical particles) and surface growth. Indeed, the predictions of the moving sectional model (Equations 3-13, 3-14 and 3-17)
reduce to those of the sectional model of Chaoul (2000) or Kumar and Ramkrishna (1997) by merely setting $\tau_{s,i} \to 0$.

Figure 3-3. Validation of the proposed moving (solid line) and fixed (open circles) sectional models by comparison with the results, on a) total non-dimensional particle number concentration, $N/N_0$, b) average primary particle diameter and c) average number of primaries per aggregate, of the detailed two dimensional sectional scheme of Xiong and Pratsinis (1993) (squares) for the standard conditions of Kruis et al. (1993; Table 2) accounting for instantaneous nucleation, coagulation and sintering of silicon particles. Predictions from the simple sectional model of Tsantilis and Pratsinis (2000) are also shown (diamonds).
3.4.2. Flame Temperature and Precursor Conversion

Figure 3-4 shows the evolution of the gas temperature $T$ (K) along the flame as measured by FTIR spectroscopy for an inlet TTIP flow-rate of 11 g/h. Initially, the temperature increases as CH$_4$ and TTIP are consumed, while later on it decreases rapidly as it is typically seen in similar premixed flame configurations (Arabi-Katbi et al., 2001). At the filter location (20 cm downstream from the burner tip), the temperature approaches room conditions (~300 K) following a rather linear profile. More specifically, for the needs of the present study a piecewise linear temperature profile is used consisting of: $T = 7248.56 \cdot x + 423$ (for 0.0 cm $\leq x \leq 0.3$ cm), $T = -146.69 \cdot x + 2641.57$ (for 0.3 cm $\leq x \leq 6.5$ cm) and $T = -102.82 \cdot x + 2356.43$ (for 6.5 cm $\leq x \leq 20$ cm).

Figure 3-4. Conversion (%) of TTIP by thermal decomposition (as an overall reaction) for an inlet TTIP flowrate of 11 g/h (solid line), along with the corresponding gas temperature profile measured by FTIR. TTIP conversion is complete within the first 0.4 cm from the burner tip. The temperature at the filter location (20 cm from the burner tip) is approximately 300 K.
The evolution of the overall (%) conversion of TTIP to TiO$_2$ by thermal decomposition is also shown in Figure 3-4. The conversion of TTIP is practically completed rather fast, approximately within the first 0.38 cm from the burner tip. This is also supported by FTIR showing no TTIP peaks down to approximately 0.4 cm. It should be clarified here that Figure 3-4 reports the conversion of TTIP as dictated by thermal decomposition as an overall reaction pathway including the partial (and additive) contributions of gas phase and surface growth thermal decomposition reactions, as shown earlier in case (C). In other words, (when hydrolysis is excluded) whether surface growth is the dominant reaction mechanism or not, the conversion of TTIP to TiO$_2$ is still the same and always governed by thermal decomposition. Therefore, the rate of formation of TiO$_2$ by TTIP is the same in cases (A) and (C) while the surface growth coefficient $k_s$ is restricted by the equation: $k_g = k - A \cdot k_s \cdot \rho_g$, that is when $k < A \cdot k_s \cdot \rho_g$ (at high aerosol area concentrations A) $k_g$ is set equal to 0 and $k = A \cdot k_s \cdot \rho_g \Rightarrow k_s = k/(A \cdot \rho_g)$. The conversion of TTIP by hydrolysis is not shown simply because the reaction is so fast that is practically instantaneous. This alternative reaction path (Seto et al., 1995; Kashima and Sugiyama, 1990) should be treated with caution as the corresponding reaction rate (provided here in lack of any other relevant data) is typically used at moderate temperatures (i.e., 673 K) in the abundance of water (molar ratio H$_2$O:TTIP > 10). Furthermore, when thermal decomposition (with or without surface growth) is combined with hydrolysis, TTIP conversion is the same as for hydrolysis only.

### 3.4.3. Integral Aerosol Dynamics and Comparison with Experimental Data

Figure 3-5 depicts the evolution of the total (aggregate) particle number concentration, $N$, for thermal decomposition in the absence (broken line) and presence (solid line) of surface growth as well as hydrolysis (dash and dot line) for 11 g/h TTIP and the temperature history described in Figure 3-4. When surface reaction is neglected the particle number concentration increases as long as gas phase thermal decomposition is the dominant growth mechanism. At about 0.17 cm from the burner tip, the conversion of TTIP is approximately 50%. It is at this point where the total number concentration starts to decrease as the competing coagulation mode becomes equally important. Higher, up to ~0.4
cm the decrease of N is steep since it is within that range that high temperatures still prevail (Figure 3-4) and the conversion of the precursor is completed. From that point on, there is no compensation for the loss of particles by collisions and thus coagulation proceeds at gradually lower rates. Similar trends are observed in the presence of surface growth (solid line). TTIP is now consumed both in the gas phase and on the surface of newly formed titania particles. Although surface growth does not alter the overall conversion rate of the precursor, and thus the total monomer mass accumulation, it does narrow down the active region of gas phase thermal decomposition which is the sole source of the particle number population. Therefore, in this case the particle number concentration is in general smaller and becomes comparable with the one for pure gas phase thermal decomposition only after ~2 cm away from the burner, at a region where coagulation takes over completely.

Figure 3-5. Theoretical evolution of titania aggregate particle total number concentration (N: particles/g_{gas}) as predicted, for the same conditions as in Figure 3-4, by the proposed moving sectional model accounting for sintering (Kobata et al., 1991) and A) gas phase thermal decomposition in the absence of surface growth (broken line), B) hydrolysis (dash and dot line), C) gas phase thermal decomposition in the presence of surface growth (solid line). The highest value of N is encountered for case (B) at x \rightarrow 0.
It should be pointed out that under the present process conditions and the effect of surface growth, the gas phase chemical reaction mode is confined very fast (within the first 0.04 cm) which is reflected on the initially sharp increase of the particle number concentration (solid line in Figure 3-5). This is also why here, in contrast to Chaoul (2000) and Spicer et al. (2002), there is no secondary "nucleation burst" which is typically encountered at lower reaction rates when the pure gas phase chemical reaction mode can almost balance the number population reduction by coagulation for a second time (thus resulting in a local minimum in the evolution of the average particle diameter). Finally, the lowest particle number concentrations are encountered for the case of hydrolysis (case B). This is expected as the employed hydrolysis reaction rate is so high that the depletion of the TTIP precursor is virtually instantaneous. Thus, a large particle monomer population is momentarily \( (at x \rightarrow 0) \) formed which immediately later on “shrinks” by rapid coagulation.

\[
*n_{p,av} = \bar{N}_l n_{p,av}/\sum N_l
\]

Figure 3-6. Theoretical evolution of the average number of titania primary particles per aggregate as predicted, for the same conditions as in Figure 3-4, by the proposed moving sectional model accounting for sintering (Kobata et al., 1991) and A) gas phase thermal decomposition in the absence of surface growth (broken line), B) hydrolysis (dash and dot line), C) gas phase thermal decomposition in the presence of surface growth (solid line).
The simulation results in Figure 3-5 can be better understood in Figure 3-6 showing the evolution of the average number of primary particles per aggregate, $n_{p,av}$, for the three reaction pathways considered in the present study and the same conditions as in Figure 3-4. More specifically, for the case of hydrolysis (dash and dot line), large aggregate structures are predicted close to the burner face, stemming from the almost instant consumption of the TTIP precursor, even at relatively low temperatures ($< 500$ K). Under these conditions coagulation becomes faster than sintering and aggregate particles are eventually formed (Tsantilis et al., 2001). Further downstream ($x > 0.2$ cm) and as the flame process temperature increases, full coalescence takes place. Nevertheless, as the temperature steadily decreases (Figure 3-4), sintering times (Kobata et al., 1991) increase and a point is reached, at $x > 6$ cm, where aggregation takes over again. Moreover, the sharp increase of $n_{p,av}$ encountered in the far downstream region of the flame reactor (Figure 3-6, dash and dot line) along with the flat total area concentration profile observed at the same location, imply the attainment of a critical primary particle size, above which primary particle growth practically stops.

Within the same context, the initial $n_{p,av}$ values for thermal decomposition, in the absence (case A, broken line) and presence (case C, solid line) of surface growth, are considerably lower than for hydrolysis as the employed overall thermal decomposition rate is significantly smaller than that of the latter case. Close to the burner face, the prevailing low flame temperatures ($< 500$ K) allow only for a limited conversion of the TTIP precursor to TiO$_2$ by thermal decomposition, thus promoting the formation of spherical particles. Then, as the gas phase chemical reaction mode is quickly replaced by pure surface growth ($k_g = 0$ and $k_s = k/(A \cdot \rho_g)$, at approximately 0.04 cm), the $n_{p,av}$ for case (C) acquires a slightly smaller local maximum than in case (A). In other words, this may stem from the fact that in case (C) the initial gas phase chemical reaction mode ($k_g = k - A \cdot k_s \cdot \rho_g$) is smaller than the one ($k_g = k$) employed in case (A). Similar trends to hydrolysis are later followed further downstream. Finally, far away from the flame source ($x > 10$ cm) where conditions of almost pure agglomeration occur ($\tau_{s,i} \rightarrow \infty$), the aerosol with the highest number concentration will produce the highest $n_{p,av}$. 
Figure 3-7. Experimental Sauter mean titania primary particle diameter (circles) as a function, for the same conditions as in Figure 3-4, of the vertical position above the burner along with predictions from the proposed moving sectional model accounting for sintering (Kobata et al., 1991) and A) gas phase thermal decomposition in the absence of surface growth (broken line), B) hydrolysis (dash and dot line), C) gas phase thermal decomposition in the presence of surface growth (solid line). The bars are one standard deviation below and above the experimental average primary particle diameter. The experimental point at 20 cm (filter location) is based on BET measurements, while the experimental points at lower locations are derived from image analysis of TEM pictures by counting more than 1000 primary particles.

Figure 3-7 shows the evolution of the Sauter mean primary particle diameter as predicted by the proposed moving sectional model for the three available chemical reaction schemes, and the same conditions as in Figure 3-4, along with experimental measurements. The bars around the experimental data points are one standard deviation of the size distribution below and above the average primary particle diameter. The experimental point at 20 cm (filter location) is based on BET measurements (of samples from the filter), while
the experimental points at lower locations are derived from image analysis of TEM pictures by counting more than 1000 primary particles per point to assure that the estimations are statistically correct. The primary particle size evolution for pure gas phase TTIP thermal decomposition (case A, broken line) steadily overpredicts the experimental data, thus indicating that this chemical reaction mechanism is not the appropriate one.

As also shown in previous studies (Pratsinis and Spicer, 1998; Chaoul, 2000), when the contribution of surface growth is important, the average particle size becomes higher. Here however, this is the case only till $x = 0.28$ cm. In detail, up to approximately $0.07$ cm, pure gas phase thermal decomposition produces smaller primaries with a higher degree of aggregation (Figures 3-6 and 3-7) than does surface growth. Later on ($0.07$ cm $< x < 0.2$ cm), as the flame process temperature increases, sintering as well as surface growth are enhanced and primary particles, for both cases (A and C), start to grow faster (Figures 3-6 and 3-7, solid and broken lines). Nevertheless, the gas phase chemical reaction mode in case (A) is more significant than in case (C), thus sustaining much higher particle number concentrations and coagulation rates (Figure 3-5) which in turn account for the sharp increase of the (primary) particle diameter to values even higher than those for surface growth (at $x > 0.28$ cm). This trend continues even after the complete depletion of the TTIP precursor ($x \approx 0.4$ cm) and levels off only when low sintering rates reoccur.

In contrast to case (A), the model predictions for thermal decomposition and surface growth (case C, solid line) are in good agreement with their experimental counterparts. This can be an indication that surface growth plays indeed a significant role in the present process in agreement with the small geometric standard deviations, (Figure 3-8) typically observed in these experiments (Arabi-Katbi et al., 2001; Figure 3-9). Surface reaction of TTIP acts as a condensation-like mechanism, leading (when dominant) to narrower particle size distributions than coagulation alone (Chaoul, 2000). It is worth noticing that such an effect could not have been observed without thermophoretic sampling of titania particles along the flame, since the comparison with model predictions for instantaneous chemical reaction, coagulation and sintering, neglecting surface growth (case B), is also fairly good at locations further away ($x > 1$ cm) from the burner face where coagulation is already the dominant mechanism. Nevertheless, close to the burner tip, hydrolysis leads to a
considerable overprediction of the first two experimental data. This trend can be attributed to a possible overestimation of the actual reaction as the currently available in the open literature hydrolysis reaction rate is based on the assumption of rather high initial water to TTIP ratios (> 10).

3.4.4. Evolution of Primary Particle Size Distribution

Additional comparisons between experimental data and model predictions regarding the detailed primary particle size distributions and the corresponding geometric standard deviations, at different locations along the flame, can provide a better insight of the process under investigation. Figure 3-8, depicts the evolution of the (number-based) geometric standard deviation of the gas stream primary particle size distribution as predicted by the present moving sectional model, for the same conditions as in Figure 3-4, along with experimental results from image analysis of TEM pictures. The predictions for pure gas phase thermal decomposition (broken line) are considerably higher than their experimental counterparts and definitely above the self-preserving limit (1.46) for free-molecular coagulation, in the full coalescence region between ~0.15 cm and ~6 cm. The onset of full coalescence between 0.1 cm and 0.2 cm (Figure 3-6) momentarily decreases the width of the gas stream primary particle size distribution (Figure 3-8, local minimum of broken line). Soon afterwards, the peak of the $\sigma_{g,p}$ at about 2.8, reveals the occurrence of bimodal distributions attributed to the competition between chemical reaction and coagulation modes (Tsantilis and Pratsinis, 2000).

As observed in the previous figure, the agreement with experimental data is improved when accounting for surface growth (solid line) or even hydrolysis (dash and dot line). More specifically, in the region between approximately 0.25 cm and 0.4 cm, where coalescence is complete and surface growth is dominant, the $\sigma_{g,p}$ for the case of surface growth is smaller than that for hydrolysis. Close to the burner face, hydrolysis keeps the $\sigma_{g,p}$ at low levels (virtually monodisperse), within a distance which is more extended than in the other two reaction model cases, as the combination of slow sintering and fast collision events theoretically keeps the primary particle size close to monomer dimensions. Finally, irrespective of which reaction path is chosen, the $\sigma_{g,p}$ (for $x \rightarrow 20$ cm) asymptotically
approaches values corresponding to a rather monodisperse gas stream primary particle size distribution which is in agreement with earlier studies (Vemury et al., 1994; Tsantilis and Pratsinis, 2000) showing that such a trend can be attributed to the particle size dependence of the specific sintering time (Kobata et al., 1991) namely, \( \tau_{s,i} \sim d_{p,i}^4 \). This trend however, appears to be artificially enhanced under the assumption of a single particle area per volume size interval (one dimensional sectional model), especially for conditions of pure agglomeration \( (\tau_{s,i} \to \infty, A = \text{constant}) \) of initially polydisperse particles, here encountered at approximately more than 9 cm above the burner tip.

![Figure 3-8](image)

*Figure 3-8. Experimental (number based) geometric standard deviation of (gas stream) titania primary particles (circles) as a function, for the same conditions as in Figure 3-4, of the vertical position above the burner along with predictions from the proposed moving sectional model accounting for sintering (Kobata et al., 1991) and A) gas phase thermal decomposition in the absence of surface growth (broken line), B) hydrolysis (dash and dot line), C) gas phase thermal decomposition in the presence of surface growth (solid line).*

Figure 3-9 shows comparisons between experimental data (circles) and model predictions of gas stream primary particle size distributions for purely gas phase thermal
decomposition (broken lines), gas phase hydrolysis (dash and dot lines) and thermal decomposition with surface growth (solid lines), at three different locations along the flame: a) 0.5 cm, b) 2.3 cm and c) 5.5 cm, for the conditions of Figure 3-4. Emphasis is given at the lower heights in the flame as there the effects of the different chemical reaction schemes are more direct (not blurred by coagulation). It is now explicitly shown that pure gas phase chemical reaction produces much wider distributions than experimentally observed (broken lines). It should be noted here that although the main count modes (Hinds, 1999) show that theory (broken lines) underpredicts the experimental data (circles), this is not the case for the Sauter mean diameters (Figure 3-7) as they typically tend to represent points closer to the right tail of the distribution. Moreover, there is still some slight degree of bimodality even after the end of the reaction (Figure 3-9, broken lines). The narrow peak (representing only a small fraction of the total distribution and appearing at particle sizes approximately bigger than 60 nm) marks the threshold above which sintering is very slow, and gradually fades away for x > 6 cm. Thus, although the average number of primary particles per aggregate is (for instance, at x = 0.5 cm) almost 1, the secondary peak in the distribution indicates the presence of a small number of primaries that are not fully coalesced but parts of bigger aggregates. This is also why comparisons between model predictions and their experimental counterparts in terms of any average size, give only a first indication of the actual trends and not the whole picture of events.

As for hydrolysis (dash and dot lines), distributions are fairly close to the experimental ones (in shape), but shifted to bigger size ranges (especially at 0.5 cm). The disagreement at 0.5 cm is mainly attributed to the abrupt collapse of large aggregates into spherical particles in the presence of high collision rates subsequently taken over by fast sintering (Figure 3-7, dash and dot line). The best results are obtained with surface growth (solid lines). Simulations are fairly close to experimental data even down to 0.5 cm form the burner tip. In agreement with Chaoul (2000), surface growth, when dominant, tends to narrow down particle size distributions. Thus, at 0.5 cm (Figure 3-9a) the predicted gas stream primary size distribution is narrower than in the case of pure gas phase thermal decomposition and closer to the corresponding experimental measurements. The sharp left hand side tail of the distribution, especially at 0.5 cm (Figure 3-9a, solid line) stems from
the complete dominance of surface reaction at earlier stages \((k_g \text{ set to } 0)\) leaving practically no room for an alternative particle growth mode by nucleation and coagulation at sizes smaller than \(\sim 7.5\) nm (similar results are obtained also at an even finer grid resolution, corresponding to an initial spacing factor of 1.7). Of course, at exactly 0.5 cm the depletion of TTIP is already complete (at \(\sim 0.4\) cm). Despite that, the role of surface chemical reaction is not strictly limited during the reaction of the precursor, as also seen by Pratsinis and Spicer (1998; Figures 2 and 3) as well as Chaoul (2000), since the dynamics of particle growth have already been changed at the earlier stages. Eventually however, as coagulation takes over, chemical reaction effects gradually fade away and all model predictions come closer to each other and to the experimental data (Figure 3-9c). Furthermore, better agreement with experimental data at \(x = 0.5\) cm could arise from a combination of gas phase and surface growth (by thermal decomposition) and a new (gas phase) hydrolysis reaction rate that is not so fast as the current one and takes into account water concentration.

An additional average primary particle diameter and primary particle size distribution can be derived by TEM image analysis after transferring particles from the filter cake (at \(x = 20\) cm) into TEM grids. The Sauter-mean diameter derived from TEM analysis is 49 nm with a standard deviation of 21 nm, while the average primary particle diameter directly measured by BET is 43 nm. The corresponding experimental primary particle size distribution however, is rather wide \((\sigma_{g,p}\) around 1.59) as particles collected at the filter exhibit a residence time distribution, as they come from different radial locations across the flame representing different temperature and therefore velocity profiles. In general, a premixed flame configuration is chosen in order to avoid complex temperature and flow patterns. However, the region of uniform temperature narrows down further downstream (especially for \(x > 5\) cm) and particles with different residence times and temperature histories may consequently be included in the TEM sample (Arabi-Katbi et al., 2001). Furthermore, at \(x > 5\) cm the flame flicker increases substantially. In conclusion, a comparison of predicted \(\sigma_{g,p}\) with data at \(x > 5\) cm (till the filter), requires detailed computational fluid mechanics calculations, interfaced with aerosol dynamics (Johannessen et al., 2000).
Figure 3-9. Experimental (circles) gas stream primary particle size distributions at a) 0.5 cm, b) 2.3 cm and c) 5.5 cm distance from the flame, along with predictions from the proposed moving sectional model for sintering (Kobata et al., 1991) and purely gas phase thermal decomposition (broken line), gas phase hydrolysis (dash and dot line) and thermal decomposition with surface growth (solid line), for the same conditions as in Figure 3-4.
It is worth noticing that the results obtained from calculations carried out with a simple monodisperse model (Appendix E) accounting for simultaneous nucleation, surface growth, coagulation and sintering, are relatively close to the sectional simulations. Especially for cases (B) and (C), the predicted monodisperse mean diameters (= 6V/A) are smaller than their sectional counterparts by a maximum relative difference of about 13 %, as monodisperse coagulation rates are typically lower (Hinds, 1999). However, monodisperse calculations could have resulted in bigger errors, had the range of a dominant surface growth mode been prolonged (Chaoul, 2000). For the case of pure gas phase thermal decomposition, the maximum relative difference (for s = 2) is approximately 60 %. This big underprediction mainly results from the occurrence of bimodal distributions (Figure 3-8).

The spacing factor, s, in all the above sectional calculations is equal to 2, which is a convenient value in terms of computational efficiency (Hounslow et al., 1988). For the cases of hydrolysis and surface growth (Figure 3-10), decreasing the spacing factor from 2 to 1.5 or even 1.2 does not have a very significant effect on the results depicted in Figures 3-5 - 3-9. The primary particle size distributions become slightly narrower (Figures 3-10a and 3-10c) while the Sauter mean primary particle diameters (Figure 3-10b) decrease by less than 2 % (thus, bringing the maximum relative difference from the monodisperse models within approximately 11 %). For the case of purely gas phase thermal decomposition (Figure 3-11) the average number concentration of particles is high enough to sustain particle populations at large particle size scales. The coarser the grid is, the more difficult it becomes for aggregates in large volume size intervals to fully coalesce after collision, therefore artificially giving rise to secondary peaks in the primary particle size distributions (Figure 3-9; broken lines, 70 nm ≤ d_{p,i} ≤ 130 nm). As the spacing factor decreases, these secondary peaks gradually disappear (Figure 3-11a). Consequently, decreasing the spacing factor from 2 to 1.7, 1.5 or even down to 1.2 decreases the Sauter mean primary particle diameter by as much as 33 % at x > 10 cm, while for s < 1.2 there is no more significant change (Figure 3-11b). For instance, for s = 1.1 the maximum relative difference between sectional and monodisperse calculations is approximately 19 %, while the agreement with the experimental Sauter mean primary particle diameters is so good that
one cannot clearly distinguish which reaction mechanism is dominant by merely relying on average primary particle diameters. Nevertheless, even for $s = 1.1$, the calculated primary particle size distributions (for pure gas phase thermal decomposition) remain considerably wider than their experimental counterparts (Figure 3-11c) indicating once again that gas phase thermal decomposition alone is not the prevailing reaction path.

Figure 3-10: Effect of spacing factor, $s$, on the primary particle size distribution (at $x = 0.5$ cm) $(a)$, Sauter mean primary particle $(b)$ and primary particle geometric (number based) standard deviation $(c)$ for the cases of hydrolysis and surface growth.
Figure 3-11: Effect of spacing factor, $s$, on the primary particle size distribution (at $x = 0.5$ cm) (a), Sauter mean primary particle (b) and primary particle geometric (number based) standard deviation (c) for the case of thermal decomposition.

3.5. CONCLUSIONS

The dynamics of titania nanoparticle growth were simulated by an efficient moving sectional aerosol dynamics model accounting for simultaneous gas phase and surface reactions, coagulation and sintering in a premixed TTIP-methane-oxygen flat flame. The
model was validated by comparing it against standard sectional solutions and detailed literature models. Three different reaction pathways were investigated, namely, pure gas phase thermal decomposition, gas phase hydrolysis, and gas phase and surface thermal decomposition of TTIP to explain measured primary particle size distributions through comparisons with experimental data regarding Sauter mean primary particle diameters, geometric standard deviations and the full primary particle size distributions at different locations along the flame. It should be noted that the assumption of a monodisperse primary particle size distribution per volume interval artificially narrowed the gas stream primary particle size distributions during pure agglomeration of polydisperse particles. At the conditions studied, the best agreement between theory and data was obtained with surface growth. Comparisons between sectional and monodisperse calculations, revealed maximum relative differences (in terms of average primary particle diameters) of ~11 % for hydrolysis or surface growth and ~19 % for gas phase thermal decomposition. Finally, the present analysis can be useful for studying other processes involving gas and surface growth reactions, such as soot formation and synthesis of nanoparticles of controlled size, where monitoring the very early stages of particle formation and growth is of importance.

3.6. NOTATION LIST

- \( a \): dummy volume used in Equation D-1 (cm\(^3\))
- \( A \): total aggregate area concentration (cm\(^2\)/g\(_{\text{gas}}\))
- \( A_i \): aggregate area concentration in section i (cm\(^2\)/g\(_{\text{gas}}\))
- \( C \): concentration of TTIP (molecules/g\(_{\text{gas}}\))
- \( \text{CARS} \): Coherent Anti-Stokes Raman Spectroscopy
- \( d_{c,i} \): collision diameter (cm)
- \( D_f \): mass fractal dimension
- \( d_m \): monomer volume equivalent diameter (cm)
- \( d_{p,i} \): primary particle diameter (cm)
- \( d_{ps} \): Sauter mean primary particle diameter (cm)
- \( \text{ET} \): Emission-Transmission
- \( \text{FTIR} \): Fourier Transform Infra-Red
HAB  height above burner (cm)
k  TTIP overall thermal decomposition reaction coefficient (1/s)
k_g  TTIP gas phase thermal decomposition reaction coefficient (1/s)
k_s  TTIP surface reaction coefficient (cm/s)
N  total titania aggregate number concentration (particles/g_gas)
N_i  titania aggregate number concentration in section i (particles/g_gas)
N_o  initial number concentration of monomers used in Figure 3-3a (1/m^3)
Normrad Normalized radiance
n_p,av  average number of primary particles per aggregate
n_p,i  number of primary particles per aggregate in section i
n(v,t)  particle density function (cm^-6)
Q_r  inlet total gas flowrate at reference conditions (cm^3/s or L/min)
r_critical  critical ratio of (x_{i+1}/x_{i-1})
S  burner tube cross sectional area (cm^2)
s  (initial) spacing factor (x_{i+1}/x_i)
SiO_2  silica
t  time (s)
T  temperature (K)
TEM  Transmission Electron Microscopy
T_r  reference temperature (298 K)
T(x)  centerline temperature profile (K)
TiO_2  titania
TTIP  titanium tetra-isopropoxide: Ti(OC_3H_7)_4
v_i  lower boundary point volume bin i (cm^3)
V_i  aggregate volume concentration in section i (cm^3/g_gas)
v_m  titania molecular volume (cm^3)
v_{p,i}  primary particle volume in section i (cm^3)
u_x  average velocity (cm/s)
x_i  representative (pivot) point volume of bin i (cm^3)
x  distance from the burner tip (cm)
Greek Letters

\( \alpha_{m} \) surface area of a spherical titania molecule (cm\(^2\))

\( \alpha_{i,s} \) surface area of a completely fused titania aggregate of volume \( x_i \) (cm\(^2\))

\( \alpha_{p,i} \) surface area of a primary particle in section \( i \) (cm\(^2\))

\( \beta_{j,k} \) collision frequency (cm\(^3\)/s)

\( \delta \) Dirac delta function

\( \eta' \) non-dimensional interpolation volume fraction defined in Equation 3-11

\( \eta_i \) non-dimensional parameter defined in Equation 3-13

\( \rho_g \) carrier gas density (g/cm\(^3\))

\( \sigma \) standard deviation (nm)

\( \sigma_g \) (number based) geometric standard deviation of aggregates

\( \sigma_{g,p} \) (number based) geometric standard deviation of (gas stream) primaries

\( \tau_{s,i} \) characteristic sintering time (s)

3.7. REFERENCES


4. POPULATION BALANCE MODELING OF SYNTHESIS OF TITANIA NANOPARTICLES IN ELECTRICALLY ASSISTED PREMIXED FLAMES

ABSTRACT

Particle dynamics are investigated by population balance modeling during electrically assisted flame synthesis of titania by titanium tetraisopropoxide (TTIP) decomposition. An efficient moving sectional model earlier developed for simultaneous gas phase and surface chemical reactions, coagulation and sintering is extended to account for field and diffusion charging, electrostatic coagulation as well as particle dispersion and migration losses. The model is validated by comparing its predictions against detailed but cumbersome literature models at certain limiting cases. Good agreement is obtained between model predictions and experimental data with respect to the evolution of average primary particle diameter and size distribution for three different inlet TTIP flowrates, in the absence of electric fields and without any adjustable parameters. In the presence of electric fields the relative significance of temperature reduction and particle charging is investigated with respect to the evolution of primary particle size distributions.

4.1. INTRODUCTION

Charging of particles in electrically assisted aerosol processes can have a significant impact on product particle characteristics such as average primary particle size, degree of aggregation and crystallinity (Pratsinis, 1998). Hardesty and Weinberg (1973) showed that, during hexamethyl di-siloxane (HMDSO or (CH$_3$)$_6$Si$_2$O) oxidation in a methane-air premixed flame, increasing the intensity (from 0 to 6 kV) of an external electric field could reduce silica (SiO$_2$) average primary particle size by a factor of three. Katz and Hung (1990) reported an increase in aggregate size with increased field strength in a H$_2$ / O$_2$ counter-flow diffusion flame, used for the synthesis of silica, titania (TiO$_2$) and germania (GeO$_2$) particles.

Vemury and Pratsinis (1995) used needle electrodes to induce a gaseous electric discharge (corona) across a diffusion flame aerosol reactor to produce titania nanoparticles of reduced primary particle size and crystallinity (rutile weight content).
Similar results (with respect to primary particle size) were also observed for several configurations of needle and plate electrodes during synthesis of silica nanoparticles from silicon tetrachloride (SiCl$_4$) oxidation / hydrolysis in a premixed methane-oxygen-nitrogen flat flame (Vemury and Pratsinis, 1996), or even during synthesis of tin oxide particles (SnO$_2$) in a non-stabilized laminar premixed flame with needle electrodes (Vemury et al., 1997a).

Morrison et al. (1997) used Fourier transform infrared (FTIR) spectroscopy to measure for the first time the effects of external electric fields (induced by flat plate electrodes) across a premixed TiO$_2$-laden flame. Their measurements revealed similar particle and carrier gas temperatures as well as stronger decrease of particle concentration (in the presence of electric fields) resulting mostly from particle electrostatic dispersion rather than dilution with the surrounding air.

Kammler and Pratsinis (2000) studied the effect of external electric fields on aerosol flame synthesis of fumed silica at high production rates (up to 87 g/h). In agreement with Spicer et al. (1998) the soot content of the product powder increased with applied potential (regardless of electrode polarity).

Katzer et al. (2001) used a tandem DMA (Differential Mobility Analyzer) technique to extract particle charge distributions in a titania particle-laden methane-oxygen premixed flame in the presence of needle, sphere and plate electrode pairs. For the applied potentials (up to 4 kV/cm) sphere electrodes had the weakest effect on particle characteristics while needle electrodes increased aggregate size by up to a factor of 3. Plate electrodes caused separation of the aerosol into a positive and negative plume without injection of additional charge carriers. Most notably, the main mechanism for particle size reduction in that case was therefore suggested to stem from shifts in local temperature rather than from a primary electrostatic process (such as the slowing of coagulation by electrostatic repulsion among charged particles).

Recently, Kammler et al. (2002) used FTIR emission/transmission (E/T) spectroscopy to measure flame temperatures in a electrically assisted (with plate electrodes) premixed flat flame producing titania nanoparticles by titanium tetraisopropoxide (TTIP or Ti(OC$_3$H$_7$)$_4$) decomposition. FTIR measurements showed (in agreement with the visible reduction of flame height) that the external electric field narrowed the high temperature region of the flame and led to a steeper gradient further upstream without, however, changing the maximum flame temperature close to the
burner tip. Furthermore, the introduction of electric fields did not significantly disturb (especially for low heights above the burner tip) the radial uniformity of the temperature profiles between the electrodes.

Parallel to the above, mostly experimental, research efforts, modeling of simultaneous particle growth and charging in aerosol processes was also investigated. Adachi et al. (1981) solved the population balance equation for simultaneous electrostatic coagulation, electrostatic dispersion and Brownian coagulation assuming monodisperse particle size distributions. Their predictions were in agreement with experimental data demonstrating that electrostatic coagulation and dispersion were important for asymmetrically charged bipolar particles. In a subsequent study, Adachi et al. (1985) extended the above model by incorporating the Fuchs ion-particle combination probability function to describe, in agreement with experimental data, unipolar and bipolar particle diffusion charging.

Oron and Seinfeld (1989b) developed an elaborate two-dimensional sectional method for the calculation of size-charge distributions during simultaneous (unipolar or bipolar) charging and coagulation of ions and particles. They included also electrostatic dispersion, ion recombination as well as ion and particle production and loss, therefore combining earlier computations for the limiting cases of either low particle (Oron et al. 1989) or low ion (Oron and Seinfeld, 1989a) concentrations. Their results for the time evolution of charge distributions were consistent with earlier studies (Adachi et al., 1981).

Xiong et al. (1992) investigated the effect of ionic additives during gas phase coagulation of fine spherical titania particles from TiCl$_4$ vapor oxidation. They used a sectional technique (Xiong and Pratsinis, 1991) to solve the particle population balance equation that accounted for Coulomb's law and Maxwell's image model for calculating the repulsive forces between unipolarly charged particles. Their model predicted smaller average particle size and narrower size distributions with increased ion concentration in agreement with sparse literature data regarding the effect of ionic additives during soot formation.

Vemury et al. (1997b) studied simultaneous electrostatic dispersion and polydisperse coagulation of charged particles with initial symmetric and asymmetric charge distributions. They proposed a more simplified and computationally efficient version of the cumbersome sectional population balance model of Oron and Seinfeld
(1989a) by using the so-called mean value theorem on frequency (Hounslow et al., 1988; Kumar and Ramkrishna, 1996) rather than the mean value theorem on number density (Gelbard et al., 1980), therefore substituting the calculation of integrals in each section with a corresponding average value. Simulation results showed that symmetric bipolar charging increased the coagulation rate and particle size when particles were highly charged (with a mean of 10 charges per particle), while asymmetric bipolar charging decreased particle number concentration without leading to larger particles as electrostatic dispersion was more dominant than coagulation. Furthermore, a monodisperse (with respect to particle size) model was shown to be in reasonably good agreement with sectional calculations on both particle number concentration and average size for residence times < 200 s and high initial charge asymmetries.

Park et al. (2001) investigated the effect of electrostatic forces on the aggregation of particles in the free molecular regime by performing a Brownian dynamic simulation solving the Langevin equation (Friedlander, 2000) with periodic boundary conditions. For the calculation of the particle motion they considered thermal and electrostatic forces, while aggregate shape was described in terms of the so-called fractal dimension. Most notably, their simulation results showed more significant variations (reduction) of the fractal dimension (with increasing charge) in the unipolar case than in the bipolar one, and were thus consistent with earlier experimental observations (Hyeon-Lee et al., 1998; Vemury et al., 1997a).

Recently, Maisels et al. (2002) used a (computationally demanding) Direct Simulation Monte Carlo (DSMC) method (Kruis et al., 2000) to investigate the selectivity of aggregation in mixtures of two chemically different, bipolarly charged aerosols. Along this line, a novel approach for the estimation of an average aggregate diameter based on primary particles of different sizes was also presented. The main goal of their work was to demonstrate the optimal conditions (in terms of initial particle size and charge characteristics) for synthesis of composite aggregates containing the same number (but not necessarily mass) of primary particles of both components (bicomponent 1:1 mixed nanoaggregates).

In retrospect, there has been little work comparing efficient population balance models and detailed experimental data in electrically assisted flame aerosol synthesis. There, steep temperature gradients are typically encountered and aggregate particle formation and growth proceed alongside with chemiionization of the flame gases and
subsequent particle charge acquisition. Specifically, the objective of the present study is to investigate, the fundamental processes contributing to the evolution of titania particle size characteristics during titanium tetraisopropoxide (TTIP) decomposition in a premixed methane flame operating between a pair of flat plate electrodes (Figure 4-1). Thus, a sectional model is developed that describes particle formation by gas phase and surface growth reactions followed by coagulation and sintering of charged aggregates as well as charge acquisition, electrostatic dispersion and migration effects. The significance of the above mechanisms on product TiO$_2$ particle size will be examined by comparisons between in-house experimental data (Kammler, 2002) and model predictions of the evolution of primary particle size characteristics along the flame.

4.2. EXPERIMENTAL

The experimental set up of an electrically assisted flame aerosol reactor is described in Kammler (2002). It consists of an electric field, across a premixed methane-oxygen flat flame, sustained by a pair of parallel flat plate electrodes, each one on either side of the burner tube (5 cm apart and with their lower edge aligned approximately 0.1 cm above the burner tip). Titania particles are made by decomposition of 2, 20 and 40 g/h of TTIP, corresponding to TiO$_2$ production rates of 0.5, 5.5 and 11 g/h, respectively. Table 4-1, summarizes the input flow-rates of the carrier gases for each of the above cases. Each of the plate electrodes is 2.5 cm high, 3.8 cm wide and 0.4 cm thick. One electrode is connected to high voltage supply so that the field strength across the flame is -1.5 kV/cm, while the other one is grounded. A precision resistor is inserted between the ground electrode and the ground to measure the current across the flame (Vemury and Pratsinis, 1995). The rest of the experimental procedures (with respect to temperature measurement, and particle collection) are the same (with or without electric fields) as those described earlier in Kammler (2002). In summary, the experimental particle size data at 20 cm are based on image analysis of TEM pictures of samples from the filter, while at lower locations experimental particle size data are derived from image analysis of TEM pictures obtained from the central axis of the flame by thermophoretic sampling (TS).
**Table 4-1: Gas flow-rates and equivalence ratios (Φ: fuel / oxidizer ratio divided by the stoichiometric fuel / oxidizer ratio) of the investigated flames. Volumetric flow-rates are reported at 1 atm and 298 K (Kammler, 2002).**

<table>
<thead>
<tr>
<th>TTIP</th>
<th>TiO₂</th>
<th>Ar</th>
<th>CH₄</th>
<th>N₂</th>
<th>O₂</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/h</td>
<td>g/h</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>L/min</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.65</td>
<td>0.6</td>
<td>5</td>
<td>1.2</td>
<td>1.03</td>
</tr>
<tr>
<td>20</td>
<td>5.5</td>
<td>0.65</td>
<td>0.4</td>
<td>4.3</td>
<td>1.2</td>
<td>1.04</td>
</tr>
<tr>
<td>40</td>
<td>11</td>
<td>0.65</td>
<td>0.1</td>
<td>3.9</td>
<td>1.2</td>
<td>0.92</td>
</tr>
</tbody>
</table>

**4.3. THEORY**

**4.3.1. Reaction Model**

By comparing detailed measured and calculated size distributions during flame synthesis of TiO₂ from TTIP (in the absence of electric fields), it was shown in Tsantilis et al. (2002) that surface reaction was most likely the dominant route for early particle growth. It should be noted that the experimental system in Tsantilis et al. (2002) is exactly the same as the one in the current study (with the only exception being that of the external electric fields). In addition, the currently investigated input TTIP and carrier gas flow-rates, and flame temperatures, are in the same order of magnitude as those considered in Tsantilis et al. (2002). Therefore, it is here assumed that the depletion of TTIP still occurs by both homogeneous gas phase (Okuyama et al., 1990) thermal decomposition (Equation 3-4) as well as by thermal decomposition on the surface (Battiston et al., 1997, 1999) of existing TiO₂ particles (Equation 3-5).

**4.3.2. Charging Model**

Figure 4-1 depicts a schematic of the overall physical process expected to take place in the flame when two plate electrodes are set on either side. The curved lines between the electrodes represent possible trajectories of either positive (solid lines) or negative (broken lines) ions (Figure 4-1). Chemiionization of the flame gases (Pedersen and Brown, 1993) is conventionally considered as the only source of ions as plate electrodes inject negligible or no amount of new charges (Lawton and Weinberg, 1969). Particles are charged after colliding with the surrounding ions by diffusion and field charging mechanisms (Friedlander, 2000) and can be transported away from the flame.
region by electrostatic dispersion (Kasper, 1981) and even migration forces (Hinds, 1999).

In addition, the electric field across the flame is expected to cause segregation of the ion cloud into two rather distinct regions, each one of a dominant positive or negative polarity (Katzer et al., 2001). As a result of the initial electro-neutrality of the flame gases and the fact that the electrical mobilities and molecular weights of typical positive and negative ions are very similar (Adachi et al., 1985), it is assumed that the region confined between the electrode plates is symmetric (Figure 4-1). In other words, particles inside the electric field are considered to be unipolarly charged by ions of average properties (that is of properties stemming from the averaging of positive and negative, singly charged ions).

![Figure 4-1: Schematic of the overall physical process expected to take place in the flame when two plate electrodes are set on either side. The curved lines between the electrodes represent possible trajectories of either positive (solid lines) or negative (broken lines) ions. The electrode on the right is negatively charged, attracting positive ions and repulsing negative ones. Thus, the ion cloud between the electrodes becomes rather symmetric about the centerline (dash and dot line), with most of the positive ions on the right and most of the negative ones on the left.](image)

It should be stressed here that unipolar charging (by either positive or negative ions) is induced by the external electric field, the absence of which would lead to rather symmetric bipolar charging with generally minor effects on particle coagulation (Matsoukas, 1997), especially when the average charge per particle is low (Adachi et al., 1981). Finally, for simplicity, particle charging effects (electrostatic coagulation, dispersion and migration) above the plate electrodes are neglected as the overall aerosol
charge distribution emerging after mixing both sides of the flame (dominated by either positive or negative ions at the earlier stages) is expected to rapidly acquire a symmetric type of form with a rather low degree of charging (Katzer et al., 2001).

4.3.3. Moving Sectional Aerosol Dynamics Model

Based on the above described reaction and charging schemes, the aerosol dynamics model adopted here is a moving sectional model (Tsantilis et al., 2002) including the additional effects of particle charge acquisition by simultaneous diffusion and field charging as well as electrostatic particle coagulation, dispersion and migration. More specifically, the evolution of the particle number concentration $N_i$ (particles/kg), in a given section $i$, is:

$$\frac{dN_i}{dt} = \frac{dN_i}{dt}_{\text{nuc}} + \frac{dN_i}{dt}_{\text{agg}} - \frac{dN_i}{dt}_{\text{disp}} - \frac{dN_i}{dt}_{\text{migr}} \quad (4-1)$$

The first right hand side (RHS) term represents birth of particles by gas phase chemical reaction (homogeneous nucleation) as titania particles in aerosol processes are typically formed in the absence of a nucleation barrier (Xiong and Pratsinis, 1991), and is given in Tsantilis et al. (2002).

The second RHS term in Equation 4-1 is the particle number evolution by coagulation (Kumar and Ramkrishna, 1996, 1997) also defined in detail in the previous chapter. In addition, the Brownian collision frequency function, spanning over the free-molecular, transition, and continuum regimes (Fuchs, 1964; Seinfeld, 1986), is corrected for electrostatic coagulation (Matsoukas, 1997) to account for the repulsive forces between unipolarly charged aerosols:

$$\beta_{j,k} = \beta_{j,k}^o \cdot \exp \left( -\frac{e^2 q_j q_k}{2 \pi \varepsilon_o (d_{c,j} + d_{c,k}) k_B T} \right) \quad (4-2)$$

where $\beta_{j,k}^o$ (m$^3$/s) is the collision kernel in the absence of electrostatic effects, $e$ is the charge of an electron ($1.6 \times 10^{-19}$ C), $q_j$ is the number of charges per aggregate in section $j$, $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J/K), and $\varepsilon_o$ ($8.85 \times 10^{-12}$ C$^2$/N/m$^2$) is the permitivity (dielectric constant) of the carrier gas (air). The effect of aggregate structure on the coagulation rate, is considered by incorporating, in the collision frequency function $\beta_{j,k}$ (including its correction for charged particles) the so called collision diameter (Kruis et al., 1993; Tsantilis and Pratsinis, 2000):
\[
d_{\text{c},i} = d_{p,i} \left( n_{p,i} \right)^{D_f} \tag{4-3}
\]

where \( d_{p,i} (m) = \left( 6N_i x_i / A_i \right) \) is the primary particle diameter in an aggregate of volume \( x_i \), \( n_{p,i} = A_i^3 / (36\pi x_i^2 N_i^3) \) is the number of primary particles within that aggregate and \( A_i \) (\( m^2/kg \)) is the aggregate area concentration in section \( i \). Moreover, \( D_f \) is the mass fractal dimension ranging from 1 to 3 for chain-like or spherical aggregates, respectively. Here, a typical value of \( D_f = 1.8 \) is used (Seto et al., 1997). This value is kept constant throughout the calculations as fractal dimensions quickly attain (Akhtar et al., 1994) a constant value determined by the collision mechanism (Schaefer and Hurd, 1990).

The last two RHS terms in Equation 4-1 represent the loss of charged particles by electrostatic dispersion and migration, respectively. Thus, for electrostatic dispersion (Kasper, 1981; Vemury et al., 1997):

\[
\frac{dN_i}{dt} \bigg|_{\text{disp}} = \frac{b_i e^2 N_i q_i^2}{\varepsilon_o} \sum_{j=1}^{M} N_j q_j \rho_g \tag{4-4}
\]

where \( b_i (s/kg) = C_c / (3\pi\mu d_{c,i}) \) is the mechanical mobility (Hinds, 1999), \( C_c \) is the Cunningham slip correction factor (Hinds, 1999), and \( \mu \) (kg/m/s) is the carrier gas viscosity. It should be noted that both \( b_i \) and \( C_c \) are now given as functions of the aggregate collision diameter. For particle losses to the electrode plate by electrostatic migration (Hinds, 1999):

\[
\frac{dN_i}{dt} \bigg|_{\text{migr}} = \frac{u_{E,i}}{L} N_i \tag{4-5}
\]

where \( L \) (m) is the half distance between the two plate electrodes, and \( u_{E,i} \) (m/s) = \( q_i e E b_i \) is the migration velocity (Hinds, 1999) for an electric field strength \( E \) (V/m).

The evolution of the particle area concentration \( A_i \) (\( m^2/kg \)), in section \( i \), is:

\[
\frac{dA_i}{dt} = \frac{dA_i}{dt} \bigg|_{\text{mac}} + \frac{dA_i}{dt} \bigg|_{\text{agg}} + \frac{dA_i}{dt} \bigg|_{\text{surf}} - \frac{dA_i}{dt} \bigg|_{\text{sint}} - \frac{dA_i}{dt} \bigg|_{\text{disp}} - \frac{dA_i}{dt} \bigg|_{\text{migr}} \tag{4-6}
\]

where the additional third and forth RHS terms account, respectively, for area increase by surface growth and area reduction by sintering. The detailed formulas for gas phase chemical reaction, aggregation, surface growth and sintering are given in Tsantilis et al. (2002). Finally, similar to Equations 4-4 and 4-5, the dispersion and migration effects are given by:

\[
\frac{dA_i}{dt} \bigg|_{\text{disp}} = \frac{b_i e^2 A_i q_i^2}{\varepsilon_o} \sum_{j=1}^{M} N_j q_j \rho_g \quad \frac{dA_i}{dt} \bigg|_{\text{migr}} = \frac{u_{E,i}}{L} A_i \tag{4-7}
\]
The number of charges per aggregate (in each section i), for simultaneous field and diffusion charging in the region between the plate electrodes is (Lawless, 1996):

\[
\frac{dq_i}{dt} = \begin{cases} 
F_i \left( \frac{\varepsilon w_i}{4} \left( 1 - \frac{v_i}{\varepsilon' w_i} \right)^2 + F_{w_i} \left( \frac{1}{1 + \kappa_i} \right) \right) & \text{if } v_i \leq \varepsilon' w_i \\
F_i \cdot F_{w_i} \left( \frac{v_i - \varepsilon' w_i}{\exp(v_i - \varepsilon' w_i) - 1 + \kappa_i \exp(v_i - \varepsilon' w_i)} \right) & \text{if } v_i > \varepsilon' w_i 
\end{cases} 
\]  
(4-8a)

where

\[
F_i = \frac{2 \pi d_{c,i} k_B T \rho_{g}}{\varepsilon} , \quad \varepsilon' = 1 + 2 \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) , \quad v_i = \frac{q_i e^2}{2 \pi \varepsilon_o d_{c,i} k_B T} , \quad w_i = \frac{e d_{c,i} E}{2 k_B T} 
\]  
(4-8b)

\[
\kappa_i = \frac{2 - \frac{\varepsilon}{3} \varepsilon_i K_{ni}}{3 \varepsilon_i u_i} = \frac{\varepsilon_i 2 \lambda_i}{3 d_{c,i} z_i E} , \quad F_{w_i} = \begin{cases} 
1 & \text{if } w_i \geq 0.525 \\
\left( w_i + 0.475 \right)^{0.575} & \text{if } w_i < 0.525 
\end{cases} 
\]  
(4-8c)

where \( \varepsilon = 50 \) is the average dielectric constant of titania (Xiong et al., 1992), \( \xi \) is the sticking probability of ion-particle collisions (here assumed equal to 1), \( \varepsilon_i \) is the ionic thermal velocity (Adachi et al., 1985; Equation 22), \( \lambda_i \) is the ionic mean free path (Adachi et al., 1985; Equation 23), \( K_{ni} = 2 \lambda_i / d_{c,i} \), and \( z_i \) (m²/V/s) is the ion electrical mobility (Adachi et al., 1985), \( N_{i\text{on}} \) (ions/kg) is the number concentration of ions in the gas and \( u_i \) (m/s) = \( z_i E \) is the ionic drift velocity. For non-isothermal conditions the ion mobility is given as (Hardesty and Weinberg, 1973) \( z_i = z_i \left( T / T_r \right) \), where \( T_r = 298 \) K and \( z_i = 1.65 \times 10^{-4} \) m²/V/s (Adachi et al., 1985) assuming an average molecular weight of ions equal to 0.1155 kg/mol (Adachi et al., 1985). Finally, the average ion concentration in the flame region between the plate electrodes can be approximated by (Lawton and Weinberg, 1969):

\[
N_{i\text{on}} = \frac{I}{e z_i E S_p \rho_g} 
\]  
(4-9)

where \( I \) (C/s) is the current across the flame and \( S_p \) (m²) is the plate electrode surface area.

Similar to Tsantilis et al. (2002) (Equations 3-16 and 3-17), a moving sectional discretization for surface growth (Kumar and Ramkrishna, 1997) and nucleation (Chaoul, 2000; Spicer et al., 2002) is also adopted here in order to avoid numerical diffusion and preserve both mass and numbers when surface reactions and nucleation
take place. Therefore, the system of differential equations to be solved includes Equations 3-1, 3-17, 4-1, 4-6 and 4-8 while the grid regeneration principles remain virtually the same as in Tsantilis et al. (2002) (a complete code is given in Appendix H). Equations 3-1, 3-17, 4-1, 4-6 and 4-8 are further transformed into a spatial coordinate mode and readily integrated using the differential equation software DGEAR (IMSL, 1980). Typically, in a premixed flame configuration, radial temperature profiles are rather uniform (Arabi-Katbi et al., 2001, Kammler et al., 2002) indicating a rather narrow residence time distribution (especially close to the burner tip), thus:

\[
\frac{dF}{dt} = \frac{dF}{dx} \frac{dx}{dt} = \frac{dF}{dx} u_x \quad (F = C, N_i, A_i, x_i, q_i)
\]

where \(u_x\) (m/s) is the gas velocity which for the case of a premixed flat flame can be approximated as (Ehrman et al., 1998; Kanury, 1982):

\[
u_x = \frac{Q_r T(x)}{S T_r}
\]

where \(S\) (m\(^2\)) is the cross sectional area of the premixed burner, \(Q_r\) (m\(^3\)/s) the total inlet gas volumetric flow-rate (defined at 1 atm and \(T_r = 298\) K) and \(T(x)\) (K) is the axial temperature profile.

### 4.3.4. Monodisperse Aerosol Dynamics Model

A monodisperse version of the above sectional model is also presented here as it is an attractive method by means of simplicity, computational efficiency and satisfactorily good accuracy (Kruis et al., 1993; Vemury et al., 1997; Spicer et al., 2002). Thus, the evolution of the number concentration of aggregates \(N\) (aggregates/kg) will be given by (now dropping the subscript \(i\)):

\[
\frac{dN}{dt} = k_e C - \frac{1}{2} \beta N^2 \rho_g - \frac{b}{e} e^2 q^2 N^2 \rho_g - \frac{u_e}{L} N
\]

The first RHS term accounts for the gain of particles by gas phase chemical reaction. The second RHS term represents the loss of particles by coagulation, while the third and forth RHS terms are relevant to particle losses by electrostatic dispersion and migration, respectively. The collision kernel \(\beta\) (m\(^3\)/s) is also given by Equation 4-2 for subscript \(j = k\).

Likewise, for the evolution of the total particle area concentration, \(A\) (m\(^2\)/kg):
\[
\frac{dA}{dt} = k_g C_{\alpha_m} + 4\pi N_n d_p (k_s C_{\rho_g}) v_m - \frac{1}{\tau_s} (A - N \alpha_s) - \frac{b q^2 e^2}{\varepsilon_o} A N \rho_g - \frac{u_E}{L} A \tag{4-13}
\]

while for the total particle volume concentration \( V \) (m\(^3\)/kg):

\[
\frac{dV}{dt} = k_g C v_m + (k_s C \rho_g) v_m - \frac{b q^2 e^2}{\varepsilon_o} V N \rho_g - \frac{u_E}{L} V \tag{4-14}
\]

Each term in Equations 4-13 and 4-14 is easily recognizable by comparison with the corresponding sectional formulations. Equations 4-12, 4-13 and 4-14 are solved simultaneously along with Equation 3-1, after applying the same transformations as above (Equations 4-10 and 4-11).

### 4.3.5. Post Processing of Results

In the following sections, predictions of the sectional model will be discussed in terms of average diameters and geometric standard deviations. In order to assure consistent comparisons between predictions from a wide variety of methods, including sectional and monodisperse calculations as well as BET measurements and counts from TEM pictures, the average particle diameter used here is the Sauter mean primary particle diameter (Hinds, 1999):

\[
d_{ps} = \left( \frac{6 \sum_i N_i \cdot x_i}{\sum_i A_i} \right) = \left( \frac{\sum_i N_i \cdot n_{p,i} \cdot d_{p,i}^3}{\sum_i N_i \cdot n_{p,i} \cdot d_{p,i}^2} \right) \tag{4-15}
\]

Finally, the geometric standard deviation (of the aggregates) is derived from Landgrebe and Pratsinis (1990; Equations B[4] and B[7]) using the density function (Kumar and Ramkrishna, 1997):

\[
n(v, t) = \sum_i N_i \cdot \delta(v - x_i) \tag{4-16}
\]

and thus

\[
\ln^2 \sigma_g = \frac{1}{9} \int_0^\infty n(v, t) \ln^2 \left( \frac{v}{v_g} \right) \, dv = \frac{1}{9} \sum_i N_i \ln^2 \left( \frac{x_i}{v_g} \right) \tag{4-17}
\]

where

\[
N = \int_0^\infty n(v, t) \, dv = \sum_i N_i \quad \text{and} \quad \ln v_g = \int_0^\infty n(v, t) \ln v \, dv = \sum_i N_i \ln x_i \tag{4-18}
\]
For the primary particles, the geometric volume, \( v_{p,g} \), and geometric standard deviation, \( \sigma_{g,p} \), are derived from equations 4-18 and 4-17 by replacing \( N_i \) with \( N_i \cdot n_{p,i} \), \( N = \sum_i N_i \) with \( \sum_i N_i \cdot n_{p,i} \cdot v \), and \( x_i \) with \( v_{p,i} = \frac{\pi d_{p,i}^3}{6} \).

4.4. RESULTS AND DISCUSSION

4.4.1. Validation

A direct comparison of the present sectional model with other sectional formulations in the open literature for electrostatic coagulation (Oron and Seinfeld, 1989b; Vemury et al., 1997) is not sought at this stage, as in contrast to the latter models, the proposed sectional scheme does not a-priori account for a specific particle charge distribution, but for a dynamic particle charge acquisition by diffusion and field charging effects (Equation 4-8). Nevertheless, comparisons can be carried out for certain limiting cases (Tsantilis et al., 2002). More specifically, the predictions (mainly, in terms of integral properties) of the current (1D) sectional model (developed in particle volume coordinates) were shown to be in good agreement with those of the detailed but cumbersome (2D) scheme of Xiong and Pratsinis (1993) (developed in particle volume and area coordinates), typically used as a standard model for coagulation and sintering (Tsantilis et al., 2002). Here, comparisons in terms of detailed gas-stream primary and aggregate particle size distributions are also discussed.

Figures 4-2 and 4-3 show predictions (solid lines) of aggregate particle size distributions from the 2D sectional calculations of Jeong and Choi (2001; Table 5) (using the model of Xiong and Pratsinis, 1993) for isothermal coagulation and sintering of SiO\(_2\), in the absence (Figure 4-2) or presence (Figure 4-3) of gas phase SiCl\(_4\) decomposition. When the present model is used without any modifications (i.e., on the collision kernel) it predicts narrower aggregate particle size distributions especially in the absence of chemical reaction (Figures 4-2 and 4-3, dash-double-dot lines). However, the collision kernel in Jeong and Choi (2001) depends on a surface fractal dimension and an aggregate surface area accessibility factor (Xiong and Pratsinis, 1993) rather than a single mass fractal dimension (Tsantilis and Pratsinis, 2000; Tsantilis et al., 2002). Hence, the agreement with the calculations of Jeong and Choi (2001) improves considerably when exactly the same coagulation rate as in Jeong and Choi (2001) is employed (Figures 4-2 and 4-3, dash-dot lines).
Figure 4-2: Aggregate particle size distributions from the 2D sectional (solid line) calculations of Jeong and Choi (2001) and the present 1D model (using two different collision kernels) for isothermal ($T = 1800$ K) coagulation and sintering of $\text{SiO}_2$, in the absence of gas phase $\text{SiCl}_4$ decomposition and electric fields.

Figure 4-3: Aggregate particle size distributions from the 2D sectional (solid line) calculations of Jeong and Choi (2001) and the present 1D model (using two different collision kernels) for isothermal ($T = 1750$ K) coagulation and sintering of $\text{SiO}_2$, in the presence of gas phase $\text{SiCl}_4$ decomposition and no electric fields.
Figure 4-4: Experimental data (open circles) of aggregate particle size distributions regarding synthesis of TiO₂ from TTIP gas phase chemical reaction, coagulation and sintering, at a maximum reaction temperature of 1473 K and two different locations inside an aerosol furnace reactor (Nakaso et al., 2001; Figure 9-2a) along with predictions from the 2D discrete-sectional model of Nakaso et al. (2001) (thin lines), and the present sectional model (thick lines).

Nakaso et al. (2001) developed a discrete sectional version of the 2D sectional model of Xiong and Pratsinis (1993) and compared simulation results on coagulation and sintering of TiO₂ (from TTIP or TiCl₄ decomposition) with experimental data in a tubular hot wall reactor. Figure 4-4 shows their model predictions (thin lines) and experimental data (open circles) for aggregate particle size distributions regarding synthesis of TiO₂ from TTIP at a maximum reaction temperature of 1473 K and two different locations inside the aerosol furnace reactor (Nakaso et al., 2001; Figure 9-2a). The predictions of the present sectional model, for the limiting case of precursor gas phase chemical reaction, coagulation and sintering and without any further modifications (thick lines), are in good agreement with those of Nakaso et al. (2001).
Figure 4-5: Experimental data (filled circles) of primary particle size distributions regarding synthesis of TiO$_2$ from TTIP gas phase chemical reaction, coagulation and sintering, at a maximum reaction temperature of 1473 K and two different locations inside an aerosol furnace reactor (Nakaso et al., 2001; Figure 9-2a) along with predictions from the 2D discrete-sectional model of Nakaso et al. (2001) (thin lines), and the present sectional model (thick lines).

Nevertheless, the corresponding primary particle size distributions (Figure 4-5, thick lines) are narrower not only with respect to their experimental counterparts (Figure 4-5, filled circles) but also with respect to the predictions of Nakaso et al. (2001) (Figure 4-5, thin lines). This trend is consistent with earlier observations (Tsantilis et al., 2002) showing that the narrowing of primary particle size distributions can be artificially enhanced under the assumption of a single particle area per volume size interval (one dimensional sectional model), especially for conditions of pure agglomeration ($\tau_{a,i} \to \infty$, $A = \text{constant}$, $d_{ps} = \text{constant}$, and $n_p > 1$) of initially polydisperse particles.
Figure 4-6: Aggregate area concentration (broken line), primary particle Sauter mean diameter (solid line) and average number of primary particles per aggregate (dash and dot line) as predicted by the present sectional model, regarding titania particle growth by simultaneous gas phase and surface TTIP reactions followed by coagulation and sintering in the premixed methane flame of the present study and in the absence of electric fields, for an inlet TTIP flowrate of 20 g/h and the same temperature profile as in Figure 4-9 (open diamonds).

For instance, this is clearly demonstrated in Figures 4-6 and 4-7 regarding titania particle growth by simultaneous gas phase and surface TTIP reactions followed by coagulation and sintering in the premixed methane flame of the present study and in the absence of electric fields. Although pure agglomeration starts to evolve at approximately 8 cm above the burner tip (Figure 4-6), the corresponding primary particle size distribution continues to narrow more, even beyond x = 8 cm (Figure 4-7). This stems from the assignment of a (single) average primary particle diameter (\(d_{p,i} = 6x_i/\alpha_i\)) in each volume size interval regardless of the initial polydispersity of the constituent primary particles.
Figure 4-7: Primary particle size distributions as predicted by the present sectional model for the same conditions as in Figure 4-6.

Figure 4-8 shows the evolution of the gas-stream primary particle geometric standard deviation ($\sigma_{gp}$, solid line) along with the ratio (dash and dot line) of the characteristic sintering time ($\tau_s \sim d_{ps}$) over the characteristic collision time, $\tau_c = 2/(\beta \cdot N \cdot \rho_g)$ (Tsantilis et al., 2001), for the same conditions as in Figure 4-6. The above ratio is used here as a mathematical tool of tracking down the onset of pure agglomeration ($\tau_s / \tau_c > 1$ and $A = \text{constant}$) and consequently the region of applicability of the present model with respect to the prediction of primary particle size distributions or their corresponding geometric standard deviations. For the case of 20 g/h TTIP, pure agglomeration of polydisperse particles manifests itself at approximately 8 cm above the burner tip (Figures 4-6 and 4-8). For $x > \sim 8$ cm, particles collide but do not coalesce at all (thus, giving rise to the formation of soft agglomerates), leaving the primary particle size distribution unchanged. Therefore, the correct evolution of $\sigma_{gp}$ in the region between $\sim 8$ and 20 cm above the burner tip (Figure 4-8, upward gray diagonal patterned lines) should be a straight line corresponding to a value of approximately 1.4.
The same procedure has been used for all primary particle size distributions and corresponding geometric standard deviations discussed in the present study (Figures 4-17 and 4-18).

![Graph showing primary particle geometric standard deviation](image)

**Figure 4-8:** Gas-stream primary particle geometric standard deviation ($\sigma_{gp}$, solid line) along with the ratio (dash and dot line) of the characteristic sintering time ($\tau_s \sim d_{ps}$) over the characteristic collision time, $\tau_c = 2/(\beta N \rho)$, as predicted by the present sectional model for the same conditions as in Figure 4-6.

### 4.4.2. Temperature Profiles

Non-intrusive temperature measurements were carried out by FTIR (Kammler et al., 2002) along the centerline of the flame. It should be noted that these temperatures represent line-of-sight measurements as the reported values are the integral values along the lines that cross the flame (from one edge to the other) through its center of axis. Figure 4-9 shows line-of-sight centerline temperatures at different locations along the premixed methane flame, for 20 g/h TTIP and no electric field (diamond cross-filled points). More accurate centerline temperatures can be derived by tomographic reconstruction (TR) of the above data (Figure 4-9, open diamonds), revealing a maximum increase of approximately 300 K (at 5 cm from the burner tip).
Figure 4-9: FTIR experimental temperature profiles (symbols) and their corresponding regression lines, along the central axis of the premixed methane flame for an inlet TTIP flowrate of 20 g/h (Table 4-1) in the absence of electric fields, with (open diamonds) or without (cross-filled diamonds) corrections by tomographic reconstruction (TR).

Figure 4-10 depicts all the (centerline) temperature profiles considered in the current investigation for 2 (triangles), 20 (diamonds) and 40 (circles) g/h TTIP, with (filled symbols) or without (open symbols) external electric fields. The temperature data reported in Figure 4-10 are higher than those in Kammler (2002), as they have been derived by multiplying the original line-of-sight experimental FTIR values (Kammler et al., 2002) by the ratio $T$ (with TR) / $T$ (without TR) earlier deduced from Figure 4-9. In lack of additional TR measurements, similar to those in Figure 4-9, the ratio $T$ (with TR) / $T$ (without TR) (for 20 g/h TTIP and no electric field) is assumed to be the same for all cases. Furthermore, the lines in Figure 4-10 are the regressions used in the present calculations (2 g/h TTIP, solid lines; 20 g/h TTIP, long broken lines; 40 g/h TTIP, short broken lines) in the presence (thick lines) or absence (thin lines) of external electric fields. Temperatures upstream the flame, typically decrease by ambient air entrainment and radiation losses (Kammler et al., 2002). The fact however that the electric field decreases the flame temperature more dramatically in the region above the
plate electrodes could be attributed to the suppression of the flame height (Kammler et al., 2002) as well as the enhanced mixing of oppositely charged ions and particles produced from the earlier segregation of the flame in the region between the electrodes (Katzer et al., 2001; Kammler, 2002). Finally, for all cases investigated in the present study (Table 4-1) with or without electric fields, the overall TTIP decomposition is complete before the first 0.7 cm above the burner tip, while gas phase chemical reaction is suppressed within the first 0.1 cm.

![Figure 4-10: FTIR temperature profiles](image)

Figure 4-10: FTIR temperature profiles (corrected by TR using the same ratio as in Figure 4-9) considered in the current investigation for 2 (triangles), 20 (diamonds) and 40 (circles) g/h TTIP, with (filled symbols) or without (open symbols) external electric fields along with the corresponding regression lines (2 g/h TTIP, solid lines; 20 g/h TTIP, long broken lines; 40 g/h TTIP, short broken lines) in the presence (thick lines) or absence (thin lines) of external electric fields.

4.4.3. Particle Growth (primary particle size distributions)

Additional comparisons between experimental data and model predictions regarding the detailed primary particle size distributions and the corresponding
geometric standard deviations, at different locations along the flame, can provide a better insight of the process under investigation. Figure 4-11 shows comparisons between model predictions (lines) and experimental primary particle size distributions (from image analysis of TEM pictures), in the presence (filled diamonds) and absence (open diamonds) of an electric field \( E = -1.5 \text{ kV/cm} \) at different locations along the flame, for a TTIP inlet flowrate of 20 g/h. It should be reminded here that Sauter mean primary particle diameters (Figures 4-13, 4-14 and 4-17) typically tend to represent points closer to the right tail of the particle size distributions (Hinds, 1999). In general, despite the complexity of the system under investigation, the agreement between model estimations and experimental measurements is satisfactorily good. In the lower sections of the flame \( (x < 5 \text{ cm}) \) differences may be amplified by uncertainties in the gas phase and surface reaction rates (Tsantilis et al., 2002). On the other hand, at \( x = 20 \text{ cm} \), experimental primary particle size distributions are wider than those theoretically calculated, as particles collected from the filter cake typically exhibit a residence time distribution as they come from various streamlines corresponding to different temperature and velocity profiles (Tsantilis et al., 2002). The most striking difference though, is the one observed at 5 cm above the burner tip in the presence of electric fields. Mixing of ions and particles of opposite charges, emerging from the segregated region between the plate electrodes (Kammler, 2002), gives rise to broader primary particle size distributions than those predicted by the present model (which neglects the above phenomenon). Small primary particles from the edges of the flame (where prevailing temperatures are relatively low) thus collide with bigger particles from the central axis. Later on, as long as the centerline temperature is high enough to sustain fast sintering of these particles, the primary particle size distribution will temporarily narrow down \( (x = 7.5 \text{ cm}) \).

For completeness, results for all the inlet TTIP flowrates investigated in the present study (Table 4-1), in terms of (number-based) geometric standard deviations of the gas stream primary particle size distributions, are also summarized in Figure 4-12 depicting predictions from the present moving sectional model (lines), along with experimental data from image analysis of TEM pictures (symbols) at different locations above the burner tip with or without electric fields.
Figure 4-11a: Experimental primary particle size distributions in the presence (filled diamonds) and absence (open diamonds) of an electric field ($E = -1.5 \text{kV/cm}$) along with model predictions (lines) at different (centerline) locations above the burner tip ($0.5 \text{cm} \leq x \leq 5 \text{cm}$) for a TTIP inlet flowrate of 20 g/h.
Figure 4-11b: Experimental primary particle size distributions in the presence (filled diamonds) and absence (open diamonds) of an electric field \( (E = -1.5 \text{ kV/cm}) \) along with model predictions (lines) at different locations above the burner tip \( (7.5 \text{ cm} \leq x \leq 20 \text{ cm}) \) for a TTIP inlet flowrate of 20 g/h.
Figure 4-12: Experimental primary particle geometric standard deviations ($\sigma_{g,p}$) for 2 (triangles), 20 (diamonds) and 40 (circles) g/h inlet TTIP flowrates, in the presence ($E = -1.5 \text{ kV/cm}$, filled symbols) or absence ($E = 0.0 \text{ kV/cm}$, open symbols) of an electric field along with the corresponding model predictions (lines) at different locations above the burner face.

More specifically, for 40 g/h TTIP and no electric fields, the underprediction of the experimental primary particle geometric standard deviation (for $x > 5 \text{ cm}$) may stem from the underestimation of flame temperatures leading to lower collision and sintering rates and in turn smaller particles (Figure 4-13) and narrower size distributions. Likewise, for 2 g/h TTIP and no electric fields, the overprediction of the experimental primary particle geometric standard deviation (for $2.5 \text{ cm} < x < 10 \text{ cm}$) may stem from the overestimation of the inlet TTIP flowrate leading to higher coagulation rates and in turn bigger particles (Figure 4-17) and wider size distributions. In general, the
experimental data (especially after the first 2.5 cm above the burner face) reveal broadening (filled versus open symbols) of the primary particle size distributions, mainly induced by enhanced fluid motion under the influence of external electric fields (Kammler, 2002). This trend is only qualitatively captured by the present model (although it neglects interactions between the centerline and neighboring streamlines) by merely accelerating the onset of pure agglomeration in the presence of electric fields, thus freezing primary particle size distributions before they are effectively narrowed by slow sintering (Tsantilis and Pratsinis, 2000; Nakaso et al., 2001).

4.4.4. Particle Growth (integral properties)

Figure 4-13 shows the axial (centerline) evolution of the Sauter mean primary particle diameter as predicted by the proposed moving sectional model for an inlet TTIP flow-rate of 20 g/h and no electric field (E = 0.0 kV/cm), along with experimental measurements (open diamonds). The bars around the experimental data points represent one standard deviation of the size distribution below and above the corresponding average primary particle diameter. When the experimental axial temperature profile is not corrected by TR (Figure 4-9, dash-double dot line), the model predictions (broken line) are in very good agreement with their experimental counterparts for up to 5 cm distance from the burner tip. Further upstream model results underpredict experimental data by approximately 24 %. Nevertheless, this deviation is reduced by almost 50 % when a more accurate temperature profile (Figure 4-9, broken line) is used after correcting the original one by TR (Figure 4-13, solid line). As the new temperatures are higher, sintering is enhanced even further away from the luminous zone of the flame leading to the formation of bigger particles. Most notably, model predictions appear to be insensitive to the above correction for the first ~ 5 cm above burner thus accounting for the good agreement between measurements and model results in earlier studies where the TR correction was not applied (Tsantilis et al., 2002).

In the far upstream region of the flame (x > ~ 8 cm) a critical primary particle size is attained, above which primary particle growth practically stops (Figure 4-13, solid line) implying the formation of soft agglomerates, in accordance with the sharp increase of the average number of primary particles per aggregate and the constant value of the total aggregate area concentration (Figure 4-6). This is also corroborated by the rather slow increase of the experimental primary diameter at locations higher than
7.5 cm above the burner tip (Figure 4-13, open diamonds). For completeness, the present sectional model can be further modified to account for the effect of dilution (Appendix F) by entrainment of cold ambient air. This effect however, leads to only a slight decrease on the evolution of the predicted Sauter mean primary particle diameter (Figure 4-13, dash and dot line).

![Figure 4-13: Experimental Sauter mean primary particle diameters (open diamonds) at different locations along the flame and predictions by the present sectional model using a temperature profile without corrections by TR (broken line) as well as with corrections by TR, with (dash and dot line) or without (solid line) dilution effects, for an inlet TTIP flowrate of 20 g/h and no electric field (E = 0.0 kV/cm). The bars around the experimental data points represent one standard deviation of the size distribution below and above the corresponding average primary particle diameter.](image)

When an electric field is applied (E = -1.5 kV/cm) between the plate electrodes (Figure 4-14), the measured current across the particle-laden flame (for the same inlet flowrates as in Figure 4-13) is \( I = 0.296 \ \mu A \) corresponding to an average ion concentration of about \( 6.7 \times 10^{11} \) ions/g-gas. According to Figure 4-14, model predictions
(solid line) in terms of Sauter mean primary particle diameters are still in good agreement with experimental data (filled diamonds). The sectional model now includes the additional effects of field and diffusion charging, electrostatic coagulation, particle dispersion and migration losses, as well as a lower flame temperature profile (Figure 4-10, filled diamonds). The monodisperse version (despite its inherent oversimplification) underpredicts the sectional calculations by less than 13 % which is consistent with earlier comparisons in the absence of electric fields (Tsantilis et al., 2002).

Figure 4-14: Experimental Sauter mean primary particle diameters (filled diamonds) at different locations along the flame in the presence of an external electric field ($E = -1.5 \text{ kV/cm}$) and an inlet TTIP flowrate of 20 g/h, along with predictions by the present sectional (solid line) and monodisperse (dash and dot line) models (using an average ion concentration deduced from the current, $I = 0.296 \mu\text{A}$, measured across the particle laden flame) as well as sectional calculations neglecting particle charging effects (dash double dot line) or using an average ion concentration deduced from the current, $I = 5.0 \mu\text{A}$, measured across the particle free flame (broken line). The bars around the experimental data points represent one standard deviation of the size distribution below and above the corresponding average primary particle diameter.
Lower temperatures decrease particle coagulation and sintering leading to the formation of smaller particles (Figure 4-13). Likewise, unipolar charge acquisition by ion-particle collisions reduces particle size through electrostatic coagulation, dispersion and migration losses. Most notably, neglecting all particle charging effects but still accounting for a reduced flame temperature (Figure 4-10, filled diamonds) leads to a primary particle size evolution (Figure 4-14, dash double dot line) virtually identical to that obtained with the additional effect of particle charging (Figure 4-14, solid line). This result (applying for all characteristics of particle growth, such as $d_{ps}$, $n_p$, $\sigma_{gp}$) demonstrates (at least for the centerline axis along the flame) the fact that temperature reduction induced by ion motion through the external electric field is a more dominant factor for controlling particle growth rather than direct particle charging, in agreement with Katzer et al. (2001) and consistent with Vemury (1996) who had pointed out that charging alone could not account for the observed reduction in particle size.

When the average ion concentration in the region between the electrodes is increased by a factor of $\sim 17$ (which corresponds to the current measured across the flame in the absence of TTIP precursor, $I = 5 \mu A$), the effect of particle charging (in addition to temperature reduction) is remarkably enhanced (Figure 4-14, broken line). Similarly, particle weight losses by electrostatic dispersion and migration increase from $\sim 12 \%$ (Figure 4-14, solid line) to $\sim 95 \%$ (Figure 4-14, broken line). Hence, this is an extreme case as the total ion concentration in the presence of particles should drop fast (Xiong et al., 1992) especially along the centerline where ion recombination effects are dominant (Lawton and Weinberg, 1969). Furthermore, as the charging model employed here (Equation 4-8) accounts only for an average (constant) ion population rather than detailed ion-ion and ion-particle interactions, a more realistic approach will be to estimate the ion number concentration from the average current across the particle-laden flame. Nevertheless, it should be noted that the above simulations should not be strictly restricted to the central axis of the flame (at least for the region where the electric field is active and close to the burner tip) as experimental temperature profiles (Kammler et al., 2002) and particle diameters appear to have small deviations in the proximity to the centerline ($\sim 0.5$ cm off center).

The minor effect of unipolar charging is better understood in Figure 4-15 depicting the evolution of the average number of charges per aggregate for two different ion concentrations, deduced from either $I = 0.296 \mu A$ (short broken line) or $I = 5 \mu A$
(solid line), along with two limiting cases (long broken lines) and a monodisperse calculation for \( I = 0.296 \, \mu\text{A} \) (dash and dot line) at the same conditions as in Figure 4-14. Indeed, the average charge per particle is smaller than one even for the extreme case of a constant high ion concentration (corresponding to \( I = 5 \, \mu\text{A} \)). Furthermore, the charging levels predicted by the monodisperse model (dash and dot line) are still in close agreement with their sectional counterparts (solid line). Charge acquisition is faster close to the burner tip (\( x < 0.24 \text{ cm} \)) as in that region, particles have a higher degree of aggregation (Figure 4-6, dash and dot line; Figure 4-18, all lines) which in turn increases the rate of ion-particle collisions.

![Figure 4-15: Average number of charges per aggregate as predicted by the present sectional and monodisperse models, along with two different particle charging limits for the same conditions as in Figure 4-14.](image)

In all cases the charging limits (long broken lines) are well above the actual charging levels. The ion limit, \( q_{\text{ion}} = E_L \varepsilon_0 A/(e\cdot N) \), represents the maximum charge required for spontaneous emission of electrons (\( E_L = 9 \times 10^8 \text{ V/m} \)) or positive ions (\( E_L = 2.1 \times 10^{10} \text{ V/m} \)) from the particle surface (Hinds, 1999). Here, even for the smallest value of particle surface field strength, \( E_L \), the ion-charging limit is never exceeded.
Similarly, the so-called Bjerrum limit (Harned and Owen, 1958), $q_B = 4\pi e_0 k_B T d_e/e^2$, represents the maximum charge per particle (or aggregate in general) above which particle neutralization by collisions with ions of opposite polarity begins. Although significantly lower than the ion limit, the Bjerrum limit is also not exceeded.

Charging levels for all the inlet TTIP flowrates investigated in the present study are shown in Figure 4-16. Similar trends are observed for all cases. In addition, the higher the inlet TTIP flowrate is, the bigger particles grow (Figure 4-17), thus acquiring more charges by collisions with the surrounding ions. Generally, the average number of charges per aggregate is less than one, meaning that not all the aggregates are charged. These low charging levels stem from the relatively low average ion concentrations in the particle-laden flames. More specifically, the average ion concentrations are in the order of $10^{11}$ ions/g-gas, while the maximum particle number concentrations (in the region between the plate electrodes) are in the order of $10^{18}$ particles/g-gas.

![Figure 4-16: Average number of charges per aggregate as predicted by the present sectional model in the presence of an external electric field ($E=-1.5$ kV/cm), using average ion concentrations deduced from current measurements in particle laden flames for all the inlet conditions investigated in the present study (Table 4-1) and the corresponding flame temperatures (Figure 4-10, thick lines).](image)
Figure 4-17 depicts the evolution of experimental Sauter mean primary particle diameters (symbols) at different locations on the central axis of the premixed methane flame in the absence (open symbols) or presence (filled symbols) of electric fields \((E = -1.5 \, \text{kV/cm})\), and for inlet TTIP flowrates of 2 g/h (triangles) and 40 g/h (circles), along with the corresponding sectional model predictions (lines). In accordance with Figures 4-13 and 4-14, data at 20 cm refer to image analysis of TEM pictures of particles directly collected from the filter and not from the centerline by TS. Hence, it should be borne in mind that these data are very likely to include the effect of mixing of various streamlines relevant to different velocity and temperature histories (Tsantilis et al., 2002). In contrast to the fairly good agreement between simulation results (thick solid line) and experimental data (filled triangles) for 2 g/h TTIP and particle charging, model predictions (thin solid line) are substantially higher than their experimental counterparts (open triangles) in the absence of electric fields. This deviation is more pronounced in the region between 5 and 10 cm above the burner tip and may stem from local inaccuracies in the measurement and subsequent correction by TR of the flame temperature (Kammler et al., 2002) as well as from possible fluctuations (typically encountered during the feed of small amounts of precursor) in the evaporation unit of the experimental set up, thus giving rise to lower than estimated TTIP inputs. This may be further substantiated by the fact that the experimental primary particle diameters in the presence of an external electric field are (contrary to 20 and 40 g/h TTIP) higher than in the absence of particle charging.

The agreement between model (thick solid line) and experimental data (filled circles) is fairly good even for the case of 40 g/h TTIP and particle charging. The experimental point at 7.5 cm (filled circle) should be treated with caution as at this location only a limited number of particles (113) was counted. However, when no electric field exists across the flame, model results (thin solid line) are significantly lower than the corresponding experimental measurements (open circles) at locations higher than 5.0 cm above the burner tip. Again, this discrepancy, especially further upstream the flame, may be attributed to local uncertainties in the measurement and subsequent correction by TR of the flame temperature (it should be noted though that in the presence of electric fields temperatures at locations higher than 5 cm above the burner tip are lower enough to accelerate the onset of pure agglomeration and render the primary particle size evolution less vulnerable to error fluctuations in temperature.
measurements). Another reason may be the fact that the present model assumes the same temperatures for particles and carrier gas (mainly air).

Figure 4-17: Experimental Sauter mean primary particle diameters at different locations along the flame in the presence (filled symbols) or absence (open symbols) of an external electric field \(E = -1.5 \text{ kV/cm}\) for inlet TTIP flowrates of 2 g/h (triangles), and 40 g/h (circles) along with predictions by the present sectional model with (thick solid lines) or without electric fields (thin solid lines). The bars around the experimental data points represent one standard deviation of the size distribution below and above the corresponding average primary particle diameter.

Recently, Lehtinen and Zachariah (2001, 2002) proposed a model regarding the effect of heat release and cooling during the growth of nanoparticles by coalescence. They showed that when particle and carrier gas temperatures were distinguished, heat release (driven by coalescence) and subsequent particle cooling by the surrounding gas, could play an important role in the evolution of particle size. Nevertheless, including the above effect into the present model makes no difference on the results (Appendix G).
Similar to 20 g/h TTIP, model predictions (both for 2 and 40 g/h TTIP) accounting only for the temperature reduction by external electric fields, are virtually the same as those accounting for this effect and the additional effects of particle charging (namely, electrostatic coagulation, dispersion and migration losses). Field effects appear to be more pronounced in the region above the plate electrodes (x > 2.6 cm) mainly because of steeper temperature gradients and earlier dispersion losses. Moreover, when the extreme case of a high constant average ion concentration (relevant to \( I = 5 \times 10^9 \) A) is considered, primary particle diameters decrease by an additional factor of approximately 28 % (with respect to what is earlier predicted using an average ion concentration deduced from current measurements across the particle-laden flames (Figure 4-17, thick solid lines)).

The degree of aggregation is another important parameter affected by the presence of electric fields. Figure 4-18 shows the evolution (along the central axis of the flame) of the average number of primary particles per aggregate, \( n_p \), with (broken lines) or without (solid lines) an external electric field (\( E = -1.5 \) kV/cm) for all the TTIP inlet flowrates investigated in the present study (Table 4-1). Regardless of particle charging and TTIP inlet flowrate, aggregate particles start to form very close to the burner tip (x < ~ 0.2 cm), as the relatively low to moderate temperatures and high particle number concentrations prevailing there, promote particle coagulation more, rather than rapid sintering (Figures 4-6 and 4-8). This trend is also in qualitative agreement with recent experimental (TEM) data (Arabi-Katbi et al., 2001; Kammler et al., 2001) and earlier sectional calculations (Tsantilis et al., 2002). With the exception of 2 g/h TTIP, the evolution of the average number of primary particles per aggregate, close to the burner face, is not affected by the presence of an electric field as in that region (x < ~ 0.2 cm) temperature profiles remain virtually undisturbed (Figure 4-10). However, for the case of 2 g/h TTIP, temperatures close to the burner are slightly lower when the electric field is active (Figure 4-10) thus, delaying TTIP decomposition and the onset of aggregation (Figure 4-18, thin broken lines). Further upstream (x > 0.2 cm) as the flame process temperature increases aggregates fully coalesce into spherical particles (\( n_p = 1 \)). Nevertheless, aggregation takes over again (\( n_p > 1 \)) following the steady decrease of temperature and sintering rate. In the presence of an electric field, (secondary) aggregate particles are encountered at lower locations along the flame, eventually reaching a higher degree of aggregation (Figure 4-
18, broken lines), consistent with TEM observations (Kammler, 2002). When dilution by entrainment of the surrounding air is taken into account, aggregates end up in considerably smaller sizes (in terms of \( n_p \)) with or without electric fields (Appendix F). Although this effect improves the agreement with TEM observations in the latter case (showing a very limited degree of aggregation far away from the burner tip, \( n_p = 1 - 3 \)), it appears to undermine the level of aggregation in the former one. It should be noted though, that in the presence of electric fields, aggregate formation can be enhanced not only by the substantial reduction of the process temperature but also by the mixing of oppositely charged particles emerging from the ion-segregated region between the electrodes. This induced motion could bring together large aggregates, consisting of small primary particles, from the edges of the flame (where temperatures are substantially lower) with less aggregated particles, consisting of bigger primaries, at the flame centerline (Kammler, 2002). Such an effect however is not considered in the present study as calculations are carried out along the central axis of the flame neglecting interactions with neighboring streamlines.

![Figure 4-18](image-url)

**Figure 4-18:** Average number of primary particles per aggregate as predicted by the present sectional model in the presence (broken lines) or absence (solid lines) of an external electric field (\( E = -1.5 \) kV/cm) for all the inlet conditions investigated in the present study (Table 4-1) and the corresponding flame temperatures (Figure 4-10).
4.5. CONCLUSIONS

The dynamics of titania nanoparticle growth were simulated by extending an efficient moving sectional aerosol dynamics model earlier developed for simultaneous gas phase and surface reactions, coagulation and sintering to account for the additional effects of field and diffusion charging, electrostatic coagulation as well as electrostatic dispersion and migration losses, in an electrically assisted premixed TTIP-methane-oxygen flat flame. The original model was further validated by comparing it against standard sectional solutions in terms of detailed particle size distributions. Comparisons with experimental data regarding Sauter mean primary particle diameters, geometric standard deviations and the full primary particle size distributions at different axial locations along the flame were carried out for three different TTIP inlet flowrates, in the presence and absence of electric fields. Monodisperse calculations, revealed maximum relative differences of ~ 13 % from sectional model results (in terms of average primary particle diameters). Despite simplifications regarding the interaction of neighboring streamlines, satisfactorily good agreement was obtained between model predictions and experimental data. The above comparisons also revealed the dominance of temperature reduction (induced by external electric fields) over direct particle charging in controlling particle formation and growth. Improved model performance (especially far away from the burner face) should include combination of aerosol dynamics and electrofluidics capturing the interaction between oppositely charged particles from various streamlines along the flame.

4.6. NOTATION LIST  (SI units, unless otherwise stated in Figures)

- \( A \) total aggregate area concentration \((m^2/k_{gas})\)
- \( A_i \) aggregate area concentration in section i \((m^2/k_{gas})\)
- \( b_i \) particle mechanical mobility in section i \((s/kg)\)
- \( C \) concentration of TTIP \((\text{molecules/kg}_{gas})\)
- CARS Coherent Anti-Stokes Raman Spectroscopy
- \( C_c \) Cunningham slip correction factor
- \( \bar{v}_i \) ionic thermal velocity \((m/s)\)
- \( d_{c,i} \) collision diameter in section i \((m)\)
- \( d_c \) average collision diameter, \(6(V/A)(A^3/(36\pi N V^2))^{(1/D)}\), \((m)\)
D\textsubscript{f} mass fractal dimension

d\textsubscript{m} monomer volume equivalent diameter (m)

\(d_{p,i}\) primary particle diameter in section \(i\) (m)

d\textsubscript{ps} Sauter mean primary particle diameter (m)

d\textsubscript{v,i} aggregate volume equivalent diameter in section \(i\) (m)

E field strength between the electrode plates (V/m)

E\textsubscript{L} particle surface field strength (V/m)

e charge of an electron (C)

ET Emission-Transmission

FTIR Fourier Transform Infra-Red

I current across the flame (A or C/s)

k TTIP overall thermal decomposition reaction coefficient (1/s)

k\textsubscript{B} Boltzmann constant (J/K)

k\textsubscript{g} TTIP gas phase thermal decomposition reaction coefficient (1/s)

k\textsubscript{s} TTIP surface reaction coefficient (m/s)

L half distance between plate electrodes (m)

N total titania aggregate number concentration (particles/kg\textsubscript{gas})

N\textsubscript{i} titania aggregate number concentration in section \(i\) (particles/kg\textsubscript{gas})

N\textsubscript{ion} ion average number concentration between the electrodes (ions/kg\textsubscript{gas})

n\textsubscript{p} number of primaries per aggregate, \(A^3/(36\pi N V^2)\), monodisperse model

n\textsubscript{p} mean number of primaries per aggregate, \((\Sigma n_{p,i}:N_i)/\Sigma N_i\), sectional model

n_{p,i} number of primary particles per aggregate in section \(i\)

n(v,t) particle density function (m\textsuperscript{-6})

q\textsubscript{B} maximum number of charges per aggregate (Bjerrum limit)

q\textsubscript{i} number of charges per aggregate in section \(i\)

q\textsubscript{Ion} maximum number of charges per aggregate (Ion limit)

Q\textsubscript{r} inlet total gas flowrate at reference conditions (m\textsuperscript{3}/s)

S burner tube cross sectional area (m\textsuperscript{2})

S\textsubscript{p} plate electrode surface area (m\textsuperscript{2})

s (initial) spacing factor (\(x_{i+1}/x_i\))

t time (s)

T temperature (K)

TEM Transmission Electron Microscopy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_r )</td>
<td>reference temperature (298 K)</td>
</tr>
<tr>
<td>( T(x) )</td>
<td>centerline temperature profile (K)</td>
</tr>
<tr>
<td>( \text{TiO}_2 )</td>
<td>titania</td>
</tr>
<tr>
<td>( \text{TTIP} )</td>
<td>titanium tetra-isopropoxide: ( \text{Ti(OC}_3\text{H}_7)_4 )</td>
</tr>
<tr>
<td>( V )</td>
<td>aggregate total volume concentration ( (m^3/kg_{\text{gas}}) )</td>
</tr>
<tr>
<td>( v_i )</td>
<td>lower boundary point volume bin ( i ) ( (m^3) )</td>
</tr>
<tr>
<td>( V_i )</td>
<td>aggregate total volume concentration in section ( i ) ( (m^3/kg_{\text{gas}}) )</td>
</tr>
<tr>
<td>( v_m )</td>
<td>titania molecular volume ( (m^3) )</td>
</tr>
<tr>
<td>( v_{p,i} )</td>
<td>primary particle volume in section ( i ) ( (m^3) )</td>
</tr>
<tr>
<td>( u_{E,i} )</td>
<td>particle migration velocity ( (m/s) )</td>
</tr>
<tr>
<td>( u_x )</td>
<td>average velocity ( (m/s) )</td>
</tr>
<tr>
<td>( x_i )</td>
<td>representative (pivot) point volume of bin ( i ) ( (m^3) )</td>
</tr>
<tr>
<td>( x )</td>
<td>distance from the burner tip ( (m) )</td>
</tr>
<tr>
<td>( z_i )</td>
<td>ion mobility ( (m^2/V/s) )</td>
</tr>
</tbody>
</table>

**Greek Letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_m )</td>
<td>surface area of a spherical titania molecule ( (m^2) )</td>
</tr>
<tr>
<td>( \alpha_{i,s} )</td>
<td>surface area of a completely fused titania aggregate of volume ( x_i ) ( (m^2) )</td>
</tr>
<tr>
<td>( \alpha_{p,i} )</td>
<td>surface area of a primary particle in section ( i ) ( (m^2) )</td>
</tr>
<tr>
<td>( \alpha_s )</td>
<td>surface area of a completely fused titania aggregate of volume ( V/N ) ( (m^2) )</td>
</tr>
<tr>
<td>( \beta_{j,k} )</td>
<td>collision frequency between particles in sections ( j ) and ( k ) ( (m^3/s) )</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Dirac delta function</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>particle relative dielectric constant (permittivity)</td>
</tr>
<tr>
<td>( \varepsilon_o )</td>
<td>carrier gas (permittivity) dielectric constant ( (C^2/N/m^2) )</td>
</tr>
<tr>
<td>( \lambda_i )</td>
<td>ionic mean free path ( (m) )</td>
</tr>
<tr>
<td>( \xi )</td>
<td>ion-particle collision sticking probability</td>
</tr>
<tr>
<td>( \rho_g )</td>
<td>carrier gas density ( (kg/m^3) )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>standard deviation ( (nm) )</td>
</tr>
<tr>
<td>( \sigma_g )</td>
<td>(number based) geometric standard deviation of aggregates</td>
</tr>
<tr>
<td>( \sigma_{g,p} )</td>
<td>(number based) geometric standard deviation of (gas stream) primaries</td>
</tr>
<tr>
<td>( \tau_c )</td>
<td>average characteristic coagulation time ( (s) )</td>
</tr>
<tr>
<td>( \tau_s )</td>
<td>average characteristic sintering time ( (s) )</td>
</tr>
</tbody>
</table>
\[ \tau_{s,i} \quad \text{characteristic sintering time of particles in section } i \text{ (s)} \]

\[ \Phi \quad \text{fuel / oxidizer equivalence ratio} \]

4.7. REFERENCES


5. OUTLOOK FOR FUTURE IMPROVEMENTS IN AEROSOL DYNAMICS MODELING

Flame processes are by far the most widely used ones for the production of ceramic commodities (such as fumed silica and pigmentary titania) or large commercially available quantities of nanoparticles in general. Though these processes are well established industrially, bringing sizable profits to the corresponding corporations, their fundamentals are not yet well understood as in typical flame reactors nanostructured powders are manufactured virtually without control at high temperatures and extremely short residence times (usually less than a second). This makes representative particle sampling and model development quite challenging. As a result, there is a great interest to better understand the basic phenomena by detailed theoretical and experimental studies so as to effectively scale up, optimally design, and precisely control aerosol flame reactors.

Within this context, the goal of the present thesis was to develop computationally efficient quantitative tools describing the effect of process variables, such as reactant concentration and process temperature, on product powder characteristics, mainly associated with average particle size, polydispersity and degree of aggregation. Monodisperse and sectional particle dynamics models were therefore proposed accounting for a variety of concurrent formation and growth mechanisms including gas phase and surface chemical reactions, coagulation, sintering, and particle charging. In general, the agreement between experimental data and model predictions was fairly good without any adjustable parameters. Nevertheless, the performance of the proposed models could be further improved.

More specifically, detailed molecular dynamics simulations (Zachariah et al., 1996) on small silica clusters and additional comparisons of sectional calculations (Xiong and Pratsinis, 1993; Tsantilis et al., 2002) with experimental data for a wide variety of process conditions should be carried out for a complete investigation of the effects and applicability of the proposed silica particle sintering time. Molecular dynamics simulations in particular have great potentiality for boosting fundamental research topics relevant to the size dependent thermodynamic properties of submicron clusters. Apart from the calculation of particle characteristic sintering times (Zachariah and Carrier, 1999) such studies could also involve the effect of phase transformation, particle coalescence heat release and subsequent cooling by radiation losses and
convection / conduction heat transfer to the surrounding gas, or even the effects of surface hydroxylation (Sheka et al., 1999), metal impurities, and particle morphology on the dynamics of small cluster interactions of the same or different materials (such as mixed oxides of TiO$_2$ and SiO$_2$). In the latter case, the topographic distribution of catalytically active sites (Espelid and Borve, 2002) in the bulk and on the surface of the particle will be of great interest.

Likewise, more accurate predictions of primary particle size distributions could be achieved (in the expense of computational power, though) by expanding the proposed sectional model described in Chapter 3 from one to two dimensions, thus covering both particle volume and surface area coordinates. Nevertheless, this should still be a more simplified and computationally efficient version of the cumbersome two-dimensional sectional population balance model of Xiong and Pratsinis (1993) as it will incorporate the so-called mean value theorem on frequency (Hounslow et al., 1988; Kumar and Ramkrishna, 1996) rather than the mean value theorem on number density (Gelbard et al., 1980), therefore substituting the calculation of integrals in each section with a corresponding average value. Alternatively, if detailed particle size distributions are not directly required, moment models (Kazakov and Frenklach, 1998; Douglas et al., 2001) providing information on integral aerosol properties including geometric standard deviations of primary and aggregate particle size distributions, constitute an increasingly attractive option. On the other hand, despite their formulation simplicity, relevant Monte Carlo simulations (Kruijs et al., 2000; Kostoglou and Konstandopoulos, 2001) are not discussed at this stage mainly because of the associated enormous computational expenses.

Finally, in industrially scaled processes of nanoparticle production there is a strong coupling of particle dynamics with fluid mechanics, usually imposed by geometric complexity and extreme process conditions (for instance, turbulent diffusion flame flows or strong external electric fields). Consequently, combining aerosol dynamics with computational fluid mechanics simulators (using commercial CFD packages for example) has tremendous potential. As a first step, qualitative information from CFD flow patterns can explain possible disagreement between theory and practice (Tsantilis et al., 1999) or provide useful insight in designing process operating conditions (Wegner et al., 2002). More detailed quantitative information regarding temperature and velocity profiles can be extracted from CFD and subsequently used
into aerosol dynamics calculations (Johannessen et al., 2000). A straightforward incorporation of full-blown aerosol dynamics models as user-defined subroutines in commercial CFD codes is nevertheless more attractive.

5.1. REFERENCES


APPENDIX A

A.1. Modification of the aerosol dynamics model for gas phase chemical reaction

If the gas phase chemical reaction of the precursor is considered, the present aerosol dynamics model (Equations 2-1, 2-2, 2-3, and 2-15) should be modified. Thus, assuming first order gas phase reaction of the precursor:

\[
\frac{dC}{dt} = -k_g \cdot C \tag{A-1}
\]

\[
\frac{dN}{dt} = -\frac{1}{2} \beta N^2 p_g - \frac{dC}{dt} \tag{A-2}
\]

\[
\frac{dV}{dt} = -\frac{dC}{dt} \cdot v_o \tag{A-3}
\]

\[
\frac{dA}{dt} = -\frac{dC}{dt} \alpha_o - \frac{1}{\tau_s} (A - N \cdot \alpha_s) \tag{A-4}
\]

where \( C \) is the precursor concentration (molecules/g\_gas), and \( A = N \cdot \alpha, V = N \cdot v \). For full coalescence, \( \tau_s \rightarrow 0 \) s.
APPENDIX B

B.1. Applicability of chemical reactions

The data of Battiston et al. (1997; 1999) were obtained in the temperature range of 660 K to 700 K. This range of course is out of the temperature range considered in the simulations of the present study. This is done in lack of other suitable data in the open literature. Indeed, to the best of our knowledge, there are no other data on formation of titania thin films, that rely on higher temperatures than those reported in Battiston et al. (1997; 1999), as the latter conditions are typically used in MOCVD processes to minimize "parasitic" reactions and particle nucleation that would contaminate the growing surface with unwanted particles.

In addition, it should be noted that both the first and second Damköhler numbers (Brodkey and Hershey, 1988), under the conditions of our study and the surface reaction rate from Battiston et al. (1997; 1999), are much smaller than 1, thus indicating that there are no mass transfer limitations in surface growth that could render the applied surface reaction kinetic model invalid. Thus, for instance at 0.3 cm from the burner top, the average particle diameter is \( d = 14.76 \text{ nm} \), the temperature is \( T = 2598 \text{ K} \), the average gas velocity \( u_x = 183.5 \text{ cm/s} \), the gas density \( \rho_g = 0.135 \times 10^{-3} \text{ g/cm}^3 \), the gas viscosity \( \mu = 0.7679 \times 10^{-3} \text{ g/cm/s} \), and the gas mean free path \( \lambda = 0.823 \times 10^{-4} \text{ cm} \). For simplicity, the properties of the gas refer to air. For a conservative calculation we assume that the diameter of the precursor (TTIP) molecule is around \( d_{\text{prec}} = 1 \text{ nm} \). For the given surface growth reaction, and particle diameter \( d \), the first Damköhler number is now defined as:

\[
D_{m1} \equiv (\text{mass transfer by chemical reaction})/ (\text{mass transfer by convection}) = \frac{d (k_s \cdot A \cdot \rho_g)}{u_x} \approx \frac{14.76 \times 10^{-7} \left(0.15857 \times 10^5 \cdot 7062.9 \cdot 0.135 \times 10^{-3}\right)}{183.5} \approx 0.12 \times 10^{-3} \ll 1
\]

For the second Damköhker number we first approximate the precursor diffusivity \( D_{\text{prec}} \) in the carrier gas using the equation (Sienfeld and Pandis, 1998: Table 12.1):

\[
D_{\text{prec}} = \frac{k_{\text{boltzmann}} \cdot T}{3 \pi \mu d_{\text{prec}}} \left[ \frac{5 + 4 \text{Kn}_{\text{prec}} + 6 \text{Kn}_{\text{prec}}^2 + 18 \text{Kn}_{\text{prec}}^3}{5 - \text{Kn}_{\text{prec}} + (8 + \pi) \text{Kn}_{\text{prec}}^2} \right] \quad \text{and} \quad \text{Kn}_{\text{prec}} = \frac{2 \lambda}{d_{\text{prec}}}.
\]

Finally, \( D_{m2} \equiv (\text{mass transfer by chemical reaction})/ (\text{mass transfer by diffusion}) = \)
\[ D_{m_2} = \frac{d^2 \left( k \cdot A \cdot p_g \right)}{D_{\text{prec}}} = \left(14.76 \times 10^{-7}\right) \left(0.15857 \times 10^5 \cdot 0.135 \times 10^{-3}\right) \approx 0.25 \times 10^{-7} \ll 1 \]

**B.2. References**


**APPENDIX C**

**C.1. Derivation of the effect of surface growth on aggregate area concentration**

The increase of particle volume concentration, in a given section i, by surface growth is (Spicer et al., 2002):

\[
\frac{dV_i}{dt}_{\text{surf}} = k_s \cdot A \cdot C \cdot v_m \cdot \rho_g \tag{C-1}
\]

\[
\frac{dV_i}{dt}_{\text{surf}} = \frac{d[N_i \cdot x_i]}{dt}_{\text{surf}} = \frac{d[N_i \cdot n_{p,i} \cdot v_{p,i}]}{dt}_{\text{surf}} = N_i \cdot n_{p,i} \cdot \frac{dv_{p,i}}{dt}_{\text{surf}}
\]

where \(v_{p,i}\) (cm\(^3\)) is the volume of a primary particle in section i. Assuming no effect of surface reaction on the particle number concentration \(N_i\) (Kumar and Ramkrishna, 1997), and number of primary particles per aggregate \(n_{p,i}\), the above equation becomes:

\[
\frac{dV_i}{dt}_{\text{surf}} = N_i \cdot n_{p,i} \cdot \frac{d\left(\frac{\pi}{6} \cdot d_{p,i}^3\right)}{dt}_{\text{surf}} = \frac{\pi}{2} \cdot d_{p,i}^2 \cdot N_i \cdot n_{p,i} \cdot \frac{d[d_{p,i}]}{dt}_{\text{surf}} \tag{C-2}
\]

Similarly, for the areas:

\[
\frac{dA_i}{dt}_{\text{surf}} = \frac{d[N_i \cdot n_{p,i} \cdot \alpha_{p,i}]}{dt}_{\text{surf}} = N_i \cdot n_{p,i} \cdot \frac{d[\pi d_{p,i}^2]}{dt}_{\text{surf}} = 2 \pi d_{p,i} \cdot N_i \cdot n_{p,i} \cdot \frac{d[d_{p,i}]}{dt}_{\text{surf}} \tag{C-3}
\]

thus, from C-1 and C-2:

\[
k_s \cdot C \cdot A_i \cdot v_m \cdot \rho_g = k_s \cdot C \cdot [N_i \cdot n_{p,i} \cdot \pi d_{p,i}^2] \cdot v_m \cdot \rho_g = \frac{\pi}{2} \cdot d_{p,i}^2 \cdot N_i \cdot n_{p,i} \cdot \frac{d[d_{p,i}]}{dt}_{\text{surf}} \Rightarrow
\]

\[
\frac{d[d_{p,i}]}{dt}_{\text{surf}} = 2 \cdot k_s \cdot C \cdot v_m \cdot \rho_g \tag{C-4}
\]

and from C-3 and C-4:

\[
\frac{dA_i}{dt}_{\text{surf}} = 2 \pi d_{p,i} \cdot N_i \cdot n_{p,i} \cdot [2 \cdot k_s \cdot C \cdot v_m \cdot \rho_g] = 4 \pi N_i \cdot n_{p,i} \cdot k_s \cdot d_{p,i} \cdot C \cdot v_m \cdot \rho_g
\]
Finally, it can be easily shown that the above formulations of \( \left. \frac{dA_i}{dt} \right|_{\text{surf}} \) and \( \left. \frac{dV_i}{dt} \right|_{\text{surf}} \) (or \( \left. \frac{dx_i}{dt} \right|_{\text{surf}} \)) do reproduce the equation \( \left. \frac{dn_{ps,i}}{dt} \right|_{\text{surf}} = 0 \).

C.2. References


APPENDIX D

D.1. Extension of the fixed sectional model of Hounslow et al. (1988) for coagulation and sintering

Considering the first mechanism of particle birth in a given section i (with boundaries \( v_{i+1} \) and \( v_i \)), by collisions between particles in the \( i-1 \) section and the \( j \) section (where \( 1 \leq j < i-1 \)), the rate of birth is given as (Hounslow et al., 1988):

\[
R_{i,j}^{(1)} = \frac{dN_{i,j}^{(1)}}{dt} = \int_{v_j}^{v_{i+1}} \beta_{i-1,j} \left( a \frac{N_{i-1}}{v_{i-1}} \right) n(a) da \cdot \rho_g \Rightarrow
\]

where \( a \) is the volume of particles in section \( j \) (\( v_j \leq a \leq v_{j+1} \)). Multiplying by \( x_i = (v_{i+1}+v_i)/2 \) and knowing that \( v_{i+1} = 2 \cdot v_i \):

\[
x_i R_{i,j}^{(1)} = x_i \frac{dN_{i,j}^{(1)}}{dt} = \frac{dV_{i,j}^{(1)}}{dt} = 3 \beta_{i-1,j} N_{i-1} N_j x_j \cdot \rho_g \quad (D-2)
\]

Summing all over \( j \):

\[
\sum_{j=1}^{i-2} x_i R_{i,j}^{(1)} = \frac{dV_i^{agg}}{dt} = \sum_{j=1}^{i-2} 3 \beta_{i-1,j} N_{i-1} N_j x_j \cdot \rho_g = 3 N_{i-1} \sum_{j=1}^{i-2} \beta_{i-1,j} V_j \cdot \rho_g \quad (D-3)
\]

Repeating the same procedure for the other three mechanisms described in Hounslow et al. (1988) and applying the volume correction factor \( k_v = 2/3 \):

\[
\frac{dV_i}{dt} \bigg|_{agg} = 2N_{i-1} \sum_{j=1}^{i-2} \beta_{i-1,j} V_j \cdot \rho_g + \beta_{i-1,i-1} V_{i-1} N_{i-1} \cdot \rho_g
\]

\[
- N_{i-1} \sum_{j=1}^{i-1} \beta_{i,j} V_j \cdot \rho_g - V_i \sum_{j=1}^{M} \beta_{i,j} N_j \cdot \rho_g 
\]

Replacing volumes with areas and adding the effect of sintering:

\[
\frac{dA_i}{dt} \bigg|_{total} = 2N_{i-1} \sum_{j=1}^{i-2} \beta_{i-1,j} A_j \cdot \rho_g + \beta_{i-1,i-1} A_{i-1} N_{i-1} \cdot \rho_g
\]

\[
- N_{i-1} \sum_{j=1}^{i-1} \beta_{i,j} A_j \cdot \rho_g - A_i \sum_{j=1}^{M} \beta_{i,j} N_j \cdot \rho_g - \frac{1}{\tau_{s,i}} \left( A_i - N_i \alpha_{i,s} \right)
\]

Finally, the system accounting for coagulation and sintering involves:

\[
\frac{dN_i}{dt} \bigg|_{agg} \quad \text{(Hounslow et al., 1988) and} \quad \frac{dA_i}{dt} \bigg|_{total} \quad (D-6)
\]
For the additional case of gas phase chemical reaction the modifications (in $dN_1/dt$, and $dA_1/dt$) are the same as in Tsantilis and Pratsinis (2000).

D.2. References


APPENDIX E

E.1. Monodisperse model for simultaneous nucleation, surface growth, coagulation and sintering

For the evolution of the total particle number concentration:

$$\frac{dN}{dt} = -\frac{1}{2} \beta N^2 \rho_g + k_g C$$  \hspace{1cm} (E-1)

For the evolution of the total aerosol volume concentration:

$$\frac{dV}{dt} = kCv_m$$  \hspace{1cm} (E-2)

For the evolution of the total aerosol surface area concentration:

$$\frac{dA}{dt} = k_g C\alpha_m - \frac{1}{\tau_s} (A - N\alpha_s) + 4\pi N_n d_p (k_g C \rho_g) v_m$$  \hspace{1cm} (E-3)

The effect of surface growth (last RHS term in Equation E-3) is derived in the same way as explicitly shown in Appendix C.
APPENDIX F

F.1. Effect of dilution by entrainment of ambient air

Dilution effects by entrainment of ambient air can be approximated through a heat balance (Holman, 1997) between two points (at locations x and x + dx, respectively) along the flame (assuming the flame gases have same properties as air):

\[ m_{j,x} \int_{T_x}^{T_{x+dx}} c_f(T) dT + m_a \int_{T_x}^{T_{x+dx}} c_f(T) dT = m_{j,x+dx} \int_{T_x}^{T_{x+dx}} c_f(T) dT \]  

where \( c_f(T) (J/K/kg) \) is the gas specific heat (Reid et al., 1987), \( T_a (= 298 \text{ K}) \) is the ambient air temperature, \( T_r (= 298 \text{ K}) \) is the reference temperature (Reid et al., 1987), \( T_x \) and \( T_{x+dx} \) are the flame temperatures at locations x and x + dx, respectively, \( m_{j,x} \) and \( m_{j,x+dx} \) (kg/s) are the flame gas mass flowrates at locations x and x + dx, respectively, and \( m_a (= m_{j,x+dx} - m_{j,x}) \) is the entrainment rate (kg/s) of ambient air. For simplicity, the above heat balance equation neglects radiation losses by \( \text{CO}_2, \text{H}_2\text{O}, \text{soot} \) and other hydrocarbons and thus the predicted amount of entrained air should be the maximum one. Since \( T_r = T_a \), Equation F-1 is further simplified as:

\[ m_{j,x+dx} = m_{j,x} \frac{\int_{T_x}^{T_{x+dx}} c_f(T) dT}{\int_{T_x}^{T_{x+dx}} c_f(T) dT} \]  

Dilution effects on precursor, particle number, area and volume concentrations are taken into account (when dT/dx < 0) by correcting these concentrations, \( W \), at each step with the ratio \( \left[ m_{j,x} / m_{j,x+dx} \right] \):

\( W_{x+dx}^{\text{corrected}} = W_{x+dx} \left[ m_{j,x} / m_{j,x+dx} \right] \) (Tsantilis et al., 1999).

When the above correction is taken into account in the sectional model presented in Chapter 4, it introduces a negligible reduction in the primary particle diameter and an equally small increase in the corresponding geometric standard deviation in the presence or absence of electric fields. Nevertheless, the impact on the evolution of the average number of primary particles per aggregate, \( n_p \), is much more significant as shown for instance in Figure F-1, for the case of 20 g/h TTIP with or without electric fields. The cases of 2 and 40 g/h TTIP follow similar trends. The reduction of \( n_p \) is more pronounced in the presence of electric fields (Figure F-1, broken and dash double-dot lines) as in that case the prevailing temperatures decline faster (Figure 4-10) thus favoring stronger entrainment of ambient air at lower locations along the flame.
Figure F-1: Effect of dilution by entrainment of ambient air on the evolution of the average number of TiO$_2$ primary particles per aggregate in a methane premixed flame with an inlet TTIP flowrate of 20 g/h (Table 4-1) in the presence or absence of electric fields, using the corresponding temperature profiles from Figure 4-10.

F.2. References


APPENDIX G

G.1. Effect of coalescence energy release on the size evolution of nanoparticles

Following up earlier molecular dynamics calculations (Zachariah and Carrier, 1999) on sintering of small silicon (Si) clusters, Lehtinen and Zachariah (2001, 2002) proposed a model regarding the effect of heat release and cooling during the growth of nanoparticles by coalescence. They showed that when particle and carrier gas temperatures were distinguished, heat release (driven by surface area reduction through coalescence) and subsequent particle cooling (through convection / conduction heat transfer with the surrounding gas and radiation), could play an important role in the evolution of particle size. Within this context, they developed a monodisperse model accounting for particle collisions, coalescence and cooling to investigate the effect of process parameters such as particle loading and pressure and concluded that in order to obtain big primary particle diameters in the absence of excessively high gas temperatures, high initial loadings and / or low pressures should be used.

Here, the effects of coalescence heat release and subsequent particle cooling are incorporated in a monodisperse model accounting for TiO₂ nanoparticle synthesis in a premixed methane flame (Tsantilis et al., 2002) by simultaneous gas and surface reactions of TTIP, coagulation and sintering (Appendix E), for the same inlet conditions and process flame temperatures as those summarized in Table 4-1 and Figure 4-10 (thin lines), respectively. More specifically, particle temperature, \( T_p \) (K), is distinguished from that of the carrier gas (air), \( T \) (K), by introducing the following equation (Lehtinen and Zachariah, 2002):

\[
c_v N_m \frac{dT_p}{dT} = \frac{\sigma_p}{\tau_s} (\alpha_s - \alpha_s) - Z \varepsilon_p \sigma_{SB} \alpha_s \left( T_p^4 - T^4 \right) \quad (G-1)
\]

where \( c_v = 9.29 \times 10^{-23} \text{ J/K/molecule} \) is the specific heat of titania particles (Holman, 1997), \( N_m \) is the number of titania monomers per (aggregate) particle, \( \sigma_p = 2.14 \text{ J/m}^2 \) is the titania particle surface energy (Xing and Rosner, 1999), \( c_g \) (J/K/molecule) is the carrier gas (air) specific heat (given as a function of \( T \) (Reid et al., 1987)), \( \varepsilon_p \approx 0.5 \) is the titania emissivity (Holman, 1997), \( \sigma_{SB} \approx 5.669 \times 10^8 \text{ W/K}^4/\text{m}^2 \) is the Stefan-Boltzmann constant, and \( Z = \alpha_s P / (2 \pi m_g k_B T)^{0.5} \) is the collision rate (1/s) between particles and carrier gas molecules with \( P \) (N/m\(^2\)) being the pressure, \( m_g \) (kg/molecule)
the carrier gas molecular weight, and $k_B (= 1.38 \times 10^{-23} \text{ J/K/molecule})$ the Boltzmann constant. The first right hand side (RHS) term in Equation G-1, represents the increase of particle temperature by coalescence energy release while the second and third RHS terms account for particle cooling by heat convection / conduction and radiation losses, respectively. Finally, the characteristic sintering time, $\tau_s$, and surface reaction constant $k_s$ are now given as functions of $T_p$ rather than $T$. Despite the above modifications, model predictions (in terms of primary particle diameters) remain unaffected. Particle and carrier gas temperatures are virtually indistinguishable throughout the flame even in the absence of radiation losses ($\varepsilon_p = 0$), while the dimensionless coalescence heating number (Lehtinen and Zachariah, 2001), $H = (\tau_0 - \tau_s)/\tau_s$, is very low (in the order of $10^{-4}$) indicating that the exothermic nature of coalescence is very weak under the current set of conditions (Table 4-1; Figure 4-10, thin lines).

A simpler, dimensionless version of the above coalescence heat release model (without radiation losses) is also given by Lehtinen and Zachariah (2001):

$$\frac{dT^*}{dt^*} = \frac{E_s}{E_b} \frac{\tau_0}{\tau_s} \alpha^* - \frac{E_g}{E_b} T^*$$

$$\frac{d\alpha^*}{dt^*} = -\frac{\tau_0}{\tau_s} \alpha^*$$

where $t^* = t/\tau_0$, $T^* = (T_p - T)/T$, $\alpha^* = (\alpha - \alpha_s)/\alpha_s$, $E_s = \sigma_p \cdot \alpha_s$, $E_b = c_v \cdot T \cdot N_m$, $E_g = \tau_0 \cdot Z \cdot c_g \cdot T$, with $\tau_0$ being the characteristic sintering time calculated at the carrier gas temperature. Figure G-1 shows the temporal evolutions (using Equations G-2 and G-3) of the particle temperature and dimensionless surface area, $\alpha^*$, for the case of two coalescing Si nanoparticles (each one having an initial diameter of 1.6 nm, consisting of 100 atoms), surrounded by Ar gas at 600 K. For this calculation, silicon has a specific heat of $c_v = 4.14 \times 10^{-23} \text{ J/K/molecule}$ (Zachariah et al., 1996) and a surface energy of $\sigma_p \text{ (J/m}^2\text{)} = 0.985 \{1+0.068(1-T_p/4000)\cdot \exp[(T_p-1500)/1500]\}$ (Zachariah et al., 1996). Although the evolution of $\alpha^*$ (Figure G-1, broken line) is similar to that reported in Lehtinen and Zachariah (2001; Figure 2a), the corresponding particle temperature (Figure G-1, solid line) reaches a maximum and then follows a fast decline in striking contrast to earlier predictions by Lehtinen and Zachariah (2001; Figure 2a) showing virtually a no particle cooling. This discrepancy however stems from an artificial underestimation of the
particle cooling rate (in the calculations of Lehtinen and Zachariah, 2002)) by a factor of 30 (Lehtinen, 2002).

Figure G-1: Temporal evolutions (using Equations G-2 and G-3) of the particle temperature and dimensionless surface area, $\alpha^s$, for the case of two coalescing Si nanoparticles (each one having an initial diameter of 1.6 nm, consisting of 100 atoms), surrounded by Ar gas at 600 K and 1 atm. If the pressure is reduced by a factor of 1000, there is no particle cooling, in accordance with Lehtinen and Zachariah (2002).

G.2. References


APPENDIX H

H.1. Moving sectional code for gas phase chemical reaction, surface growth, coagulation, sintering, and particle charging effects.

SI UNITS (unless otherwise stated)

Charging effects are eliminated by setting the ion concentration

xion = 0.0

program el20sskfltaEdilB

implicit real*8(a-h,n-z)
implicit integer*4(i-m)

parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)

dimension yp(int4num+1),y(int4num+1),rwk(10000),iwk(10000)
dimension x(intnum),v(intnum+1)
dimension betafu(intnum,intnum),xvolp(intnum)
dimension jmin(intnum,intnum+1),jmax(intnum,intnum+1)
dimension dvp(intnum+1),dbou(intnum+1)
dimension xpriv(intnum),xpriv2(intnum)
dimension xaxisp1(intnum),xaxisp2(intnum)
dimension siev(intnum,intnum),sumsiev(intnum)
dimension siev1(intnum,intnum),sumsiev1(intnum)
dimension siev3(intnum,intnum),sumsiev3(intnum)
dimension xcolidiam(intnum)
dimension xsrbdiam(intnum),xqlimH(intnum)
dimension sar(intnum+1),dsban(intnum+1)
dimension dcban(intnum+1),diol(intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmgas,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas5/a,b,c,d
common/bas6/jmin, jmax
common/bas7/v
common/bas8/ise
common/bas9/d0
common/bas10/xonethird, twothirds, fourpi, threepi, twopi
common/visc/sigmavis, epsov, xal, xb2, xc3, xe5, xf6
common/kinetic/gaspre, gase, surfpre, surfe, xx, xks, xkg
common/electric1/zaionr, xwaion, xplae, xwidth, xion, xdiel
common/electric2/xfie, xel, xeo, xet, xwpion, xwnion, xplion, zpionr
common/geometric1/vga1, dvgal
common/geometric2/vga2, dvgal2
common/dilution/xmjet, xmgas, tempjo, xmjeto

external fcn

open (unit=15,file='el20sskfltaEdilBa.txt',status='unknown')
open (unit=16,file='el20sskfltaEdilBb.txt',status='unknown')
open (unit=17,file='el20sskfltaEdilBc.txt',status='unknown')
Total distance covered (m)

tmax=20.d-2

Solver Parameters

h=1.0d-80
lrw=10000
liw=10000
ieq=int4num+1
itol=1
rtol=1.d-4
atol=1.d-45
t=0.d0
imeth=21

This is pi
vpi = 3.1415926536d0

This is the avogadro number
avog = 6.022137d23

Calculation of initial TTIP concentration ---------------------

TTIP mass consumption (g/h)
xmassttip=20.d0

Volumetric flowrates (l/min, standard)
xqAr=0.65d0
xqN2=4.3d0
xqCH4=0.4d0
xqO2=1.2d0

Molecular weights (g/mol)
xmwAr=40.d0
xmwN2=28.d0
xmwCH4=12.d0
xmwO2=32.d0
xmwTTIP=283.88d0

Universal gas constant (l*atm/mol/k)
univr=0.082d0

Reference temperature (K) and Pressure (atm)
tstand=298.d0
pstand=1.d0

Total gas mas flowrate (g/min)
xmgases=(pstand/univr/tstand)*(xqAr*xmwAr
* +xqO2*xmwO2+xqCH4*xmwCH4+xqO2*xmwO2)

For the TTIP case c0 is in moles/Kg-gas

C0=xmassttip/60.d0/xmwTTIP/xmgases*1.d3
c Constant mass fractal dimension
xdf = 1.8d0

c This is the Boltzmann constant in SI
rkb = 1.38066d-23

c This is the ideal gas law universal constant in lt*atm/mol/k
rgas = 0.082d0

c This is the pressure of 1 atm
p = 1.d0

c For MW of TiO2 particles in g/mol
xmwp = 79.9d0

c For density of TiO2 particles in kg/m3
rhop = 4.0d3

c Other constants
xonethird=1.d0/3.d0
twoothirds=2.d0/3.d0
fourpi=4.d0*vpi
threepi=3.d0*vpi
twopi=2.d0*vpi
xpisixth=vpi/6.d0
xpi=3.d0/vpi
xinvxdf=1.d0/xdf
eightandpi=8.d0+vpi
eightkb=8.d0*rkb
xpirhop=vpi*rhop
sixovpi=6.d0/vpi

c Rate constant chemical reaction (Okuyama et al., 1990)
c Activation Energy/R, in K
gase = 70.5d3/8.314d0
c Pre-exponential factor in 1/s
gaspred = 3.96d5

c Rate constant surface reaction (Battiston et al., 1997)
c Activation Energy/R, in K, look also at subroutine rate
surfe = 126.d3/8.314d0
c Pre-exponential factor in m/s, look also at subroutine rate
surfrend = 1.d9

c Data for Air (Reid, Prausnitz, and Poling, 1988)
c Air MW g/mol
xmwg = 28.8d0
c Ch./Ensg. sg in m
sigmavis = 3.711d-10
c Ch./Ensg. e/k in K
epsovk = 78.6d0
c Ch/Ensg. viscosity parameters
xa1 = 1.16145d0
xb2 = 0.14874d0
xc3 = 0.52487d0
xd4 = 0.77320d0
xe5 = 2.16178d0
xf6 = 2.43787d0

c Calculate monomer properties (TiO2) in SI
v0 = xmwp/1000.d0/(rhop*avog)
d0 = (6.d0*v0/vpi)**(1.d0/3.d0)
a0 = 6.d0*v0/d0
Electric properties
charge of an electron (C) (Hinds, 1999)
\[ x_{el} = 1.6 \times 10^{-19} \]
Permittivity (or dielectric constant)
of air or vacuum (C²/(N·m²)) (Adachi et al., 1985)
\[ x_{eo} = 8.855 \times 10^{-12} \]
Relative permittivity of titania (Xiong et al., 1992)
\[ x_{et} = 50.0 \]
correction for dielectric particles
\[ x_{diel} = 1.0 + 2.0 \times \frac{x_{et} - 1.0}{x_{et} + 2.0} \]
Reference positive ion mobility (Adachi et al., 1985), m²/V/s
\[ z_{pionr} = 1.4 \times 10^{-4} \]
Reference negative ion mobility (Adachi et al., 1985), m²/V/s
\[ z_{nionr} = 1.9 \times 10^{-4} \]
Average ion mobility, m²/V/s
\[ z_{aionr} = \frac{z_{pionr} + z_{nionr}}{2.0} \]
Molecular weight of positive ions (Adachi et al., 1985), Kg/mol
\[ x_{wpion} = 0.131 \]
Molecular weight of negative ions (Adachi et al., 1985), Kg/mol
\[ x_{wnion} = 0.100 \]
Average molecular weight, Kg/mol
\[ x_{waion} = \frac{x_{wpion} + x_{wnion}}{2.0} \]
Plate electrode surface area (m²)
\[ x_{plas} = 25.0 \times 38.0 \times 1.0 \times 10^{-6} \]
Plate height (m) (Kammler et al., 2001; submitted)
(including the 1 mm distance from the burner tip)
\[ x_{plahe} = 2.6 \times 10^{-2} \]
burner tube diameter (m)
\[ x_{dtube} = 2.5 \times 10^{-2} \]
half width between electrodes or tube diameter (m)
\[ x_{width} = \frac{50.0}{1000.0} \times \frac{1}{2.0} \]
Current across the flame (A) or (C/s)
\[ x_{ic} = 0.296 \times 10^{-6} \]
Field strength across the flame (V/m)
\[ x_{fie} = 1.5 \times 10^5 \]
Average temperature within the electrode region (K)
\[ x_{tav} = 2000.0 \]
Gas density (Kg/m³)
\[ x_{den} = p \times x_{mwg} / x_{gas} / x_{tav} \]
Temperature correction of positive ion mobility
(Hardesty and Weinberg, 1974)
\[ z_{piono} = z_{pionr} \times \left( \frac{x_{tav}}{300.0} \right) \]
Temperature correction of negative ion mobility
(Hardesty and Weinberg, 1974)
\[ z_{niono} = z_{nionr} \times \left( \frac{x_{tav}}{300.0} \right) \]
Ion concentration calculation, #/Kg-gas
\[ x_{ion} = \frac{x_{ic} \times x_{fie} \times x_{plas} \times x_{el} \times (z_{piono} + z_{niono})}{2.0} / x_{den} \]
Initialization of section positions and grid points
\[ isec = intnum - 30 \]
Volume Spacing Factor (>1)
\[ s = 1.9 \]
y(intnum+1) = v₀
\[ x(1) = y(intnum+1) \]
Initial carrier gas mass flowrate (kg-gas/s)
\[ x_{mjeto} = x_{mgases} / 60.0 / 1000.0 \]
c Initial carrier gas temperature (K)
tempjo=400.d0

c Initialize populations
y(1) = 1.d0
DO i = 2,isec
   y(i) = 0.d0
END DO

c Grid points
DO i = 2,isec
   y(i+intnum) = s*y(intnum+i-1)
x(i) = y(i+intnum)
END DO

c Grid boundaries
DO i = 2, isec
   v(i) = (y(intnum+i-1)+y(intnum+i))/2.d0
END DO
v(1) = s*y(intnum+1)-v(2)
v(isec+1) = s*y(intnum+isec)-v(isec)

c Area populations and average charge per aggregate
y(int2num+1) = a0*y(1)
y(int3num+1) = 0.d0
DO i = 2,isec
   y(int2num+i) = 0.d0
   y(int3num+i) = 0.d0
END DO

c Precursor Concentration (moles/kg-gas)
y(int4num+1) = c0

c Initialize unused x and y array space
DO i = isec+1, intnum
   y(i) = 0.d0
   y(i+intnum) = 0.d0
   y(i+int2num) = 0.d0
   y(i+int3num) = 0.d0
   x(i) = y(i+intnum)
END DO

c Determination of (j,k) classes for aggregation
IF (x(2).GE.(x(1)+x(1))) THEN
   jmin(1,1) = 1
   jmax(1,1) = 1
ELSE
   jmin(1,1) = 1
   jmax(1,1) = 0
END IF

DO i = 2,isec-1
   DO k = 1,i
      j = k
      DO WHILE(x(i-1).GT.(x(j)+x(k)))
         j = j + 1
      END DO
      jmin(i,k) = j
   END DO
   DO WHILE(((x(j)+x(k)).GT.x(i+1)).AND.(j.GE.k))
      j = j - 1
   END DO
   jmax(i,k) = j
END DO
END DO
DO k = 1,isec
  j = k
  DO WHILE(x(isec-1).GT.(x(j)+x(k)))
    j = j + 1
  END DO
  jmin(isec,k) = j
  jmax(isec,k) = isec
END DO

! Call Solver Routine
100  if (t.lt.1.d-6) then
    tend = t + 1.d-7
  elseif (t.lt.1.d-5.and.t.ge.1.d-6) then
    tend = t + 1.d-6
  elseif (t.lt.1.d-4.and.t.ge.1.d-5) then
    tend = t + 1.d-5
  elseif (t.lt.1.1d-3.and.t.ge.1.d-4) then
    tend = t + 5.d-5
  elseif (t.lt.tmax.and.t.ge.1.d-2) then
    tend = t + 5.d-6
  endif

! Additional solver parameters
rwk(1)=tend
iopt=1
rwk(5)=h
iwk(6)=10000000

call vodpk(fcn,ieq,y,t,tend,itol,rtol,atol,itask,istate,iopt,
  rwk,lrw,iwk,liw,jac,psol,imeth,1.0,1)
h=1.0d-80
itol=1
rtol=1.d-5
atol=1.d-100
istate=1

! Recalculation of grid points and section boundaries positions
DO j = 1, intnum
  x(j) = y(j+intnum)
END DO

! Recalculate the grid boundaries
DO i = 2, isec
  v(i) = (y(intnum+i-1)+y(intnum+i))/2.d0
END DO
v(1) = s*y(intnum+1)-v(2)
v(isec+1) = s*y(intnum+isec)-v(isec)

! Checking the conversion of the precursor
xconv=((c0-y(int4num+1))/c0)*100.d0

! Reorganize the grid
CALL regrid(y)

IF ((tend*100.d0).gt.0.3d0) THEN
  ! Correction of concentrations for dilution effects
  WHEN dT/dx < 0 (here for x > 0.3 cm)
  y(1+int4num) = y(1+int4num)*xmjeto/xmjet
  total1=c0*v0*avog*(xmgases/60.d0/1000.d0)/xmjet
DO idl=1, isec
  y(idl)=y(idl)*xmjeto/xmjet
  y(idl+int2num)=y(idl+int2num)*xmjeto/xmjet
END DO
END IF

WRITE(17,201) t,xmjeto,xmjet
* ,(xmjet-xmjeto)/xmjet*1.d2,temp,temp2
CALL FLUSH(17)
xmjeto=xmjeto
tempjo=temp

Then when checking the mass balance:
total2=dmoment(y,1)+y(1+int4num)*v0*avog
xerror=(total2-total1)/total1*100.d0
xerror2=((-c0*(xmgases/60.d0/1000.d0) * /xmjet-y(int4num+1))*v0*avog
* -(dmoment(y,1))/(c0*(xmgases/60.d0/1000.d0)
+ /xmjet-y(int4num+1)) * *v0*avog)*100.d0

Printing results
sumnum=0.0d0
sumare=0.0d0
sumvol=0.0d0
sumdpr=0.0d0
sumnpr=0.0d0
sumnq =0.0d0

DO i=1, isec
  x(i)=y(intnum+i)
  sumnum=sumnum+y(i)
  sumvol=sumvol+y(i)*x(i)
  sumare=sumare+y(i+int2num)
  sumnq=sumnq+y(i)*y(i+int3num)
  IF (y(i)*y(i+int2num).GT.0.d0) THEN
    sumdpr=sumdpr+y(i+int2num)**2.d0/6.0d0/vpi/x(i)/y(i)
    sumnpr=sumnpr+y(i+int2num)**3.d0/36.d0/vpi/x(i)**2.d0
      /y(i)**2.d0
    xdlp(i)=6.d0*y(i)*x(i)/y(int2num+i)
    xvolp(i)=vpi/6.d0*xdlp(i)**3.d0
  collision diameter, m
  xsoldiam(i)=xdlp(i)*((x(i)/xvolp(i))**1.d0/xdf)
  area equivalent diameter, m
  xsurdiam(i)=dsqrt(y(int2num+i)/y(i)/vpi)
  ELSE
    xsoldiam(i)=0.0d0
    xsurdiam(i)=0.0d0
  END IF
END DO

sumspa=0.0d0
DO jj=1, isec-1
  sumspa=sumspa+y(jj+1+intnum)/y(jj+intnum)
END DO

Average spacing factor
spacef=sumspa/(isec-1)

BET average diameter, in nm
dpbet=6.d0*sumvol/sumare*1.d9

Number mean primary particle diameter, in nm
\[ dpnum = \left(\frac{\text{sumdpr}}{\text{sumnpr}}\right) \times 1.0 \times 10^{-9} \]

\[ \text{diameter of average mass (or volume), in nm} \]

\[ \text{dmass} = \left(\frac{6 \text{ovpi} \times \text{sumvol} \times \text{sumnum}}{\text{sumvol} \times 2.0 \times 10^{12}}\right)^{\frac{1}{3}} \times 1.0 \times 10^{-9} \]

\[ \text{diameter of primary average mass (or volume), in nm} \]

\[ \text{dpmass} = \left(\frac{6 \text{ovpi} \times \text{sumvol} \times \text{sumnpr}}{\text{sumvol} \times 2.0 \times 10^{12}}\right)^{\frac{1}{3}} \times 1.0 \times 10^{-9} \]

\[ \text{average number of primaries per aggregate} \]

\[ xnpav = \frac{1.0 \times 36.0 \times \text{vpi}}{\text{sumare} \times 3.0 \times 10^{12} \times \text{sumvol} \times 2.0 \times 10^{12}} \]

\[ \text{average number of primaries per aggregate based on dpnum} \]

\[ xnpavn = 6.0 \times \frac{\text{sumvol} \times \text{sumnum}}{\text{vpi} \times (\text{dpnum} \times 1.0 \times 10^{-9})^{3.0 \times 10^{12}}} \]

\[ \text{mean-average number of primaries per aggregate} \]

\[ \text{xnpmean} = \frac{\text{sumnpr}}{\text{sumnum}} \]

\[ \text{mean-average charge per aggregate} \]

\[ \text{xqagav} = \frac{\text{sumnq}}{\text{sumnum}} \]

\[ \text{average charge per primary} \]

\[ \text{xqprimav} = \frac{\text{xqagav}}{\text{xnpmean}} \]

\[ \text{comparing characteristic times} \]

\[ \text{average collision radius (based on dpbet, xnpav), m} \]

\[ xracs = \frac{\text{dpbet}}{2.0 \times 1.0 \times 10^{-9}} \times (\text{xnpav})^{\frac{1}{1.0 \times df}} \]

\[ \text{average collision radius (based on dpnum, xnpav), m} \]

\[ xracn1 = \frac{\text{dpnum}}{2.0 \times 1.0 \times 10^{-9}} \times (\text{xnpavn})^{\frac{1}{1.0 \times df}} \]

\[ \text{average collision radius (based on dpnum, xnpmean), m} \]

\[ xracn2 = \frac{\text{dpnum}}{2.0 \times 1.0 \times 10^{-9}} \times (\text{xnpmean})^{\frac{1}{1.0 \times df}} \]

\[ \text{knudsen number based on xracs} \]

\[ \text{xkns} = \frac{xlm}{xracs} \]

\[ \text{knudsen number based on xracn1} \]

\[ \text{xknn1} = \frac{xlm}{xracn1} \]

\[ \text{knudsen number based on xracn2} \]

\[ \text{xknn2} = \frac{xlm}{xracn2} \]

\[ \text{diffusion coefficient based on xracs, (m2/s)} \]

\[ xdifs = \frac{\text{rkb} \times \text{temp}}{6.0 \times 10^{12} \times \text{vpi} \times \text{eta} \times \text{xracs}} \times \left(\frac{5.0 \times 10^{-9} \times xkns^2}{5.0 \times 10^{-9} \times xkns^2} + \frac{6.0 \times 10^{-9} \times xkns^2}{5.0 \times 10^{-9} \times xkns^2} + \frac{18.0 \times 10^{-9} \times xkns^2}{5.0 \times 10^{-9} \times xkns^2} + \frac{5.0 \times 10^{-9} \times xkns^2}{5.0 \times 10^{-9} \times xkns^2} \right) \]

\[ \text{diffusion coefficient based on xracn1, (m2/s)} \]

\[ xdifn1 = \frac{\text{rkb} \times \text{temp}}{6.0 \times 10^{12} \times \text{vpi} \times \text{eta} \times \text{xracn1}} \times \left(\frac{5.0 \times 10^{-9} \times xknn1^2}{5.0 \times 10^{-9} \times xknn1^2} + \frac{6.0 \times 10^{-9} \times xknn1^2}{5.0 \times 10^{-9} \times xknn1^2} + \frac{18.0 \times 10^{-9} \times xknn1^2}{5.0 \times 10^{-9} \times xknn1^2} + \frac{5.0 \times 10^{-9} \times xknn1^2}{5.0 \times 10^{-9} \times xknn1^2} \right) \]

\[ \text{diffusion coefficient based on xracn2, (m2/s)} \]

\[ xdifn2 = \frac{\text{rkb} \times \text{temp}}{6.0 \times 10^{12} \times \text{vpi} \times \text{eta} \times \text{xracn2}} \times \left(\frac{5.0 \times 10^{-9} \times xknn2^2}{5.0 \times 10^{-9} \times xknn2^2} + \frac{6.0 \times 10^{-9} \times xknn2^2}{5.0 \times 10^{-9} \times xknn2^2} + \frac{18.0 \times 10^{-9} \times xknn2^2}{5.0 \times 10^{-9} \times xknn2^2} + \frac{5.0 \times 10^{-9} \times xknn2^2}{5.0 \times 10^{-9} \times xknn2^2} \right) \]

\[ \text{particle velocity (m/s)} \]

\[ xpvelo = \text{dsqrt} \left(8.0 \times 10^{-9} \times \text{rkb} \times \text{temp} / \text{vpi} \times \text{rhop} / (\text{sumvol} \times \text{sumnum})\right) \]
c     particle mean free path, based on xracs (m)
xlpars=8.0d0*xdifs/vpi/xpvelo

c     particle mean free path, based on xracn1 (m)
xlparn1=8.0d0*xdifn1/vpi/xpvelo

c     particle mean free path, based on xracn2 (m)
xlparn2=8.0d0*xdifn2/vpi/xpvelo

c     transition parameter, based on xracs
xxgs=1.0d0/6.0d0/xracs/xlpars*
* ((2.0d0*xracs+xlparn1)**3.0d0
* -(4.0d0*xracs*xracn1+xlparn1)**(3.0d0/2.0d0))
* -2.0d0*xracs

c     transition parameter, based on xracn1
xxgn1=1.0d0/6.0d0/xracn1/xlparn1*
* ((2.0d0*xracn1+xlparn1)**3.0d0
* -(4.0d0*xracn2+xhparn2)**(3.0d0/2.0d0))
* -2.0d0*xracn1

c     transition parameter, based on xracn2
xxgn2=1.0d0/6.0d0/xracn2/xlparn2*
* ((2.0d0*xracn2+xlparn2)**3.0d0
* -(4.0d0*xracn2+xhparn2)**(3.0d0/2.0d0))
* -2.0d0*xracn2

c     collision kernel, based on xracs (m3/s)
xcols=8.0d0*vpi*xdifs/xracs/
* (xrs/(2.0d0*xracs+(dsqrt(2.0d0))*xxgs)
* +(dsqrt(2.0d0))*xdifs/xpvelo/xracs)
c     collision kernel, based on xracn1 (m3/s)
xcoln1=8.0d0*vpi*xdifn1/xracn1/
* (xracn1/(2.0d0*xracn1+(dsqrt(2.0d0))*xxgn1)
* +(dsqrt(2.0d0))*xdifn1/xpvelo/xracn1)
c     collision kernel, based on xracn2 (m3/s)
xcoln2=8.0d0*vpi*xdifn2/xracn2/
* (xracn2/(2.0d0*xracn2+(dsqrt(2.0d0))*xxgn2)
* +(dsqrt(2.0d0))*xdifn2/xpvelo/xracn2)

c     Characteristic collision time (Tsantilis et al., 2000)
c     Based on xracs, s
tchars=2.0d0/sumnum/xcols/rhog
c     Based on xracn1, s
tcharn1=2.0d0/sumnum/xcoln1/rhog
c     Based on xracn2, s
tcharn2=2.0d0/sumnum/xcoln2/rhog

c     Characteristic sintering time based on dpbet, s
tcoalb=7.4d8*temp*((dpbet*1.d-9)**4.d0)*dexp(31000.d0/temp)
c     Characteristic sintering time based on dpnum, s
tcoaln=7.4d8*temp*((dpnum*1.d-9)**4.d0)*dexp(31000.d0/temp)

c     ts/tc ratio based on xracs(dpbet,xnpav)
ratios=tcoalb/tchars
c     ts/tc ratio based on xracn1(dpnum, xnpav)
ration1=tcoaln/tcharn1
c     ts/tc ratio based on xracn2(dpnum, xnpmean)
ration2=tcoaln/tcharn2

c     Charging limits for each pivot
xelim=9.0d8
sumqH=0.d0
sumqB=0.d0

DO ich=1, isec

c     Minimum Ion charging limits (Hinds, 1999)
xqlimH(ich)=xsurdiam(ich)*xsurdiam(ich)*xelim*vpi*xeo/xel
c Bjerrum charging limits (Xiong and Pratsinis, 1992)
xqlimB(ich)=rkb*temp*xcoldiam(ich)*4.d0*vpi*xeo/xel/xel
c
Checking the charge
IF (y(int3num+ich).GT.dmin1(xqlimB(ich),xqlimH(ich))) THEN
  y(int3num+ich)=dmin1(xqlimB(ich),xqlimH(ich))
END IF
sumqH=sumqH+y(ich)*xqlimH(ich)
sumqB=sumqB+y(ich)*xqlimB(ich)
END DO
c Average ion limit for charge per aggregate
xqlimHav=sumqH/sumnum
c Average Bjerrum limit for charge per aggregate
xqlimBav=sumqB/sumnum

c OUTPUT FILES
c
x(cm),N(#/g),A(cm2/g),dSauter(nm),np,sgp,sg
WRITE(16,201)t*100.d0,sumnum/1.d3,sumare*10.d0,dpbet,xnpmean
  *,sigmagkrp(y,t),sigmagkral(y,t)
CALL FLUSH(16)

c
x(cm),q-agg-av,q-pri-av,q-agg-IonLimit,q-agg-av-Bjerrum
WRITE(21,201)t*100.d0,xqagav,xqprimav,xqlimHav,xqlimBav

c
x(cm),mass balance,dSauter(m),np
WRITE(6,201)t*100.d0,xerror2,dpbet,xnpmean
CALL FLUSH(6)

c
x(cm),mass balance,T(K),%TTIP conversion,kg(1/s)
WRITE(15,201)t*100.d0,xerror2,temp
  *(c0-y(int4num+1))/c0*1.d2,xkg
CALL FLUSH(15)

c
x(cm),sg,sgp
WRITE(23,201)t*100.d0,sigmagkral(y,t),sigmagkrp(y,t)
CALL FLUSH(23)

c
x(cm),ts/tc,ts1/tc1,ts2/tc2
WRITE(24,201)t*100.d0,rations,rations1,rations2
  *,sumare,dpbet,sigmagkrp(y,t)
CALL FLUSH(24)

c
Print intermediate APSDs and PPSDs

(x-axis: d(i), y-axis: (N(i)/Ntotal)/\Delta \ln(d(i+1)/d(i))
c
This is called INTER-IF

  ttt=t*100.d0
  IF(ttt.GT.0.09910d0.AND.ttt.LT.0.10110d0.
    OR.ttt.GT.0.49910d0.AND.ttt.LT.0.50110d0.
    OR.ttt.GT.2.40010d0.AND.ttt.LT.2.60010d0.
    OR.ttt.GT.4.90010d0.AND.ttt.LT.5.10010d0.
    OR.ttt.GT.6.90010d0.AND.ttt.LT.7.10010d0.
    OR.ttt.GT.7.90010d0.AND.ttt.LT.8.10010d0.
    OR.ttt.GT.8.90010d0.AND.ttt.LT.9.10010d0.
    OR.ttt.GT.9.90010d0.AND.ttt.LT.10.10010d0.
    OR.ttt.GT.12.90010d0.AND.ttt.LT.13.10010d0.
    OR.ttt.GT.14.90010d0.AND.ttt.LT.15.10010d0.
    OR.ttt.GT.16.90010d0.AND.ttt.LT.17.10010d0.
    OR.ttt.GT.19.90010d0) THEN

Aggregate pivot volumes
DO j = 1,isec
  x(j) = y(j+intnum)
c Primary pivot diameters, volumes, numbers and concentrations
IF ((y(j)*y(int2num+j)).GT.0.d0) THEN
  dpriv(j) = 6.d0*x(j)*y(j)/y(int2num+j)
vpriv(j) = vpi/6.d0*dpriv(j)**3.d0
  xpriv(j) = x(j)/vpriv(j)
  xtpriv(j)= xpriv(j)*y(j)
dicol(j)=dpriv(j)*(xpriv(j))**(1.d0/xdf)
ELSE
  dpriv(j) = 0.d0
  vpriv(j) = 0.d0
  xpriv(j) = 0.d0
  xtpriv(j)= 0.d0
  dicol(j) = 0.d0
END IF
END DO
c Primary particle boundary volumes and diameters
DO j = 2,isec
  vp(j) = (vpriv(j-1)+vpriv(j))/2.d0
  dvp(j) = (6.d0/vpi*vp(j))**(1.d0/3.d0)
END DO
vp(1) = s*vpriv(1)-vp(2)
dvp(1) = (6.d0/vpi*vp(1))**(1.d0/3.d0)
vp(isec+1) = s*vpriv(isec)-vp(isec)
dvp(isec+1) = (6.d0/vpi*vp(isec+1))**(1.d0/3.d0)
c Aggregate boundary volumes and volume-equiv. diameters
DO j = 2,isec
  dvban(j) = (6.d0/vpi*v(j))**(1.d0/3.d0)
END DO
c Aggregate boundary areas and area-equiv. diameters
Assuming for the areas, boundaries in the middle between pivots
Considering the first boundary as sphere:
sar(1)=vpi*(6.d0/vpi*v(1))**(2.d0/3.d0)
  dsban(1)=dsqrt(sar(1)/vpi)
do j = 2,isec
if (y(j-1).gt.0.d0.and.y(j).gt.0.0d0) then
  sar(j)=(y(j-1+int2num)/y(j-1)+y(j+int2num)/y(j))/2.d0
  dsban(j)=dsqrt(sar(j)/vpi)
else
  sar(j)=0.d0
  dsban(j)=0.d0
endif
ENDDO
For the last boundary: pivot in the middle between boundaries
if (y(isec).gt.0.d0) then
  sar(isec+1)=2.d0*y(isec+int2num)/y(isec)-sar(isec)
  dsban(isec+1)=dsqrt(sar(isec+1)/vpi)
else
  sar(isec+1)=0.d0
  dsban(isec+1)=0.d0
endif
c Aggregate boundary collision diameters
Assuming boundaries in the middle between pivots
Considering the first boundary as sphere:
dcban(1)=(6.d0/vpi*v(1))**(1.d0/3.d0)
do j = 2,isec
  dcban(j)=(dicol(j-1)+dicol(j))/2.d0
ENDDO

For the last boundary: pivot in the middle between boundaries
dcban(isec+1)=2.d0*dicol(isec)-dcban(isec)

IF (vpriv(1).LT.v(1).AND.vpriv(1).GT.0.d0) THEN
WRITE(*,*) 'PRIMARY SIZE OUT (SMALLER) OF RANGE'
STOP

------Recording of the distribution of the aggregates
------Using Volume equivalent diameters

Total number concentration of aggregates
xntotag=dmoment(y,0)

Printing aggregate particle size distribution (APSDs)
using the volume equivalent diameter, dv
using the area equivalent diameter, ds
using the collision diameter, dc
Location cm, dv nm, yg, ds nm, yv, dc nm, yc

DO j = 1, isec
IF (y(j).GT.0.d0) THEN
WRITE(22,201) tt, ((6.d0/vpi*x(j))**(1.d0/3.d0))*1.d9
* 'y(j)/xntotag/DLOG(dvban(j+1)/dvban(j))
* ,dsqrt(y(j+int2num)/y(j)/vpi)*1.d9
* ,y(j)/xntotag/DLOG(dsban(j+1)/dsban(j))
* ,dicol(j)*1.d9
* ,y(j)/xntotag/DLOG(dcban(j+1)/dcban(j))
CALL FLUSH(22)
ELSE
WRITE(22,201) tt, ((6.d0/vpi*x(j))**(1.d0/3.d0))*1.d9
* ,y(j)/xntotag/DLOG(dvban(j+1)/dvban(j))
* ,0.d0
* ,0.d0
* ,dicol(j)*1.d9
* ,y(j)/xntotag/DLOG(dcban(j+1)/dcban(j))
CALL FLUSH(22)
END IF
END DO

Start recording of the distribution of the primaries
Total number concentration of primaries
xnprif=xntotp(y)
xnprif=sumnpr

Plot based on primary boundary diameters
Counting the primaries in each section
DO irw=1, isec
DO jrw=1, isec
IF (dpriv(irw).LE.0.0d0) THEN
xaxisp11(irw)=0.0d0
xaxisp12(irw)=0.0d0
yaxisp1(irw)=0.0d0
siev1(irw,jrw)=0.0d0
ELSE IF (dpriv(irw).LE.dvp(jrw+1).AND
* .dpriv(irw).GE.dvp(jrw)) THEN
siev1(irw,jrw)=xtpriv(irw)/xnprif/DLOG(dvp(jrw+1)/dvp(jrw))
xln1d(irw)=DLOG(dvp(jrw+1)/dvp(jrw))
xaxisp11(irw)=(dvp(jrw+1)+dvp(jrw))/2.d0
xaxisp12(irw)=dpriv(irw)
yaxisp1(irw)=xtpriv(irw)/xnprif/xln1d(irw)
END IF
END DO
DO jrw= 1, isec
  sumsiev1(jrw)=0.d0
END DO
END DO

DO irw=1, isec
  sumsiev1(jrw)=sumsiev1(jrw)+siev1(irw,jrw)
END DO

Printing primary particle size distributions (PPSDs)
DO i = 1, isec
  Based on primary diameter boundaries
  WRITE(20,201)ttt,xaxisp12(i)*1.d9,sumsiev1(i),yaxisp1(i)
END DO

This is the end of the blockif for plotting intermediate PSDs
This is for the INTER-IF
END IF

Reinitialize beta function and other tables
DO i = 1, intnum
  xaxisp11(i)=0.0d0
  xaxisp12(i)=0.0d0
  xlnd1(i)=0.d0
  yaxisp1(i)=0.0d0
  xaxisp1(i)=0.d0
END DO
DO j = 1, i
  betafu(i,j)=0.d0
  siev1(i,j)=0.d0
  betafu(j,i)=betafu(i,j)
  siev1(j,i)=siev1(i,j)
END DO
END DO

SUBROUTINES
Differential Equations to be solved

subroutine fcn(ieq,t,y,yp,rpar,ipar)
  implicit real*8 (a-h,n-z)
  implicit integer*4(i-m)
  parameter (intnum = 70)
  parameter (int2num = 2*intnum)
  parameter (int3num = 3*intnum)
  parameter (int4num = 4*intnum)
  dimension y(int4num+1),yp(int4num+1),ipar(*),rpar(*)
  dimension x(intnum),betafu(intnum,intnum)
  dimension dyg(int4num),dyca(int4num),dycb(int4num)
  dimension jmin(intnum,intnum+1),jmax(intnum,intnum+1)
  dimension v(intnum+1),ts(intnum),xsint(intnum),xkniP(intnum)
  dimension d2(intnum),d2max(intnum),ww(intnum,intnum)
  dimension ccfP(intnum),bbP(intnum),xvteP(intnum),xrenP(intnum)
  dimension xaP(intnum),xwp(intnum),xvP(intnum),xfvwP(intnum)
  dimension xfP(intnum),xeffP(intnum),xbeoP(intnum)
  dimension xbe2P(intnum),xbe3P(intnum),DFcharP(intnum)
  dimension xdpr1(intnum),vpriml(intnum),vpl(intnum)
  dimension xnpr1(intnum),x1(intnum),xknl(intnum)
dimension bb1(intnum),dif1(intnum),c1(intnum)
dimension x11(intnum),gl(intnum),xsurf1(intnum)
dimension cl2(intnum,intnum),gl2(intnum,intnum)

common/bas1/c0,v0,a0,vpi,rrb,avog,rgas,p,temp,vel,xtube
commom/bas2/xmg,rhog,rhop,xnu,eta,xlm,conc,xf
commom/bas3/s,xshnum,xsharea,xfshvol
commom/bas4/x,betafu,dynx
common/bas5/a,b,c,d
common/bas6/jmin, jmax
common/bas7/v
common/bas8/isec
common/bas9/d0
common/bas10/xonethird,twothirds,fourpi,threepi,twopi*
*,xpisixth,xpithird,xinvv,xinvd,eightandpi,eightkb,xpirhop,sixovpi
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg
common/electric1/zalor,xial,xp,explahe,xwidth,xion,xdiel
common/electric2/xfie,xe,xeo,xe,xeo,xwpion,xwion,zpion,znionr
common/dilution/xmjet,xmgas,tempjo,xmjo

c     Clean-up the yp matrix before calculations
DO i=1, int4num+1
  yp(i)=0.d0
END DO
c     Calculate temperature and velocity profiles
CALL tempvel(t)
c     total reaction rate (1/s)
xk = gaspre*dexp(-gase/temp)
c     surface reaction rate (m/s)
xks = surfpre*dexp(-surfe/temp)
c     Calculate properties of carrier gas
CALL props
c     APPLY DILUTION WHEN dT/dx < 0
IF ((t*100.d0).gt.0.3d0) THEN
  c Thus for cp of air (79% N2, 21% O2): (kg*m2/s2)/kg/K
  cpa=(0.79d0*3.115d1+0.21d0*2.8115d1)/xmg*1.d3
  cpb=(0.79d0*1.357d-2+0.21d0*3.68d-6)/xmg*1.d3
  cp=(0.79d0*2.68d-5+0.21d0*1.746d-5)/xmg*1.d3
  cpd=(0.79d0*1.168d-8+0.21d0*1.065d-8)/xmg*1.d3
  
c     Surrounding air temperature (K)
tempin=298.d0
  c     Jet total mass flowrate (kg-gas/s)
xmjet=xmjo*(cpa*(tempjo-tempin)+cpb/2.d0*(tempjo**2.d0- *
    tempin**2.d0)+cpc/3.d0*(tempjo**3.d0-tempin**3.d0)
    +cpd/4.d0*(tempjo**4.d0-tempin**4.d0))/
    (cpa*(temp-tempin)+cpb/2.d0*(temp**2.d0- *
    tempin**2.d0)+cpc/3.d0*(temp**3.d0-tempin**3.d0)
    +cpd/4.d0*(temp**4.d0-tempin**4.d0))
  
  IF (xmjet.LT.(xmgas/60.d0/1000.d0)) THEN
    xmjet=xmgas/60.d0/1000.d0
  ENDIF
  ELSE
    xmjet=xmgas/60.d0/1000.d0
  ENDIF
conc = y(int4num+1)
IF (conc.lt.0.d0) THEN
WRITE(*,*) 'Concentration < 0'
STOP
END IF
IF (isec.GT.intnum) THEN
WRITE(*,*) 'isec > intnum'
STOP
END IF

Calculate Fuchs' beta matrix for all sections

sumdisp = 0.0d0
DO i = 1, isec
IF (((y(i+int2num)*y(i)).GT.0.d0) THEN
update x(i)
x(i)=y(i+intnum)
IF (x(i).LT.0) THEN
WRITE (*,*) i, ' ',x(i)
STOP
END IF

Calculate the primary particle diameter in each section, m
xdpr1(i) = 6.d0*x(i)*y(i)/y(int2num+i)

Calculate primary particle volume, m³
vprim1(i) = xpisixth*xdpr1(i)**3.d0

Calculate representative aggregate volume, m³
v1(i) = x(i)

Calculate number of primaries per aggregate
xnpr1(i) = v1(i)/vprim1(i)

IF (xnpr1(i).LT.1.d0) THEN
xnpr1(i) = 1.d0
xdpr1(i) = (sixovpi*x(i))**xonethird
ENDIF

Calculate representative collision diameter of interval i
x1(i) = xdpr1(i)*(xnpr1(i))**xinvxdf

Calculate surface-area aggregate diameter of interval i
xsurf1(i) = dsqrt(y(int2num+i)/y(i)/vpi)

Knudsen number
xkn1(i) = 2.d0*xlm/x1(i)

calculate "Brownian Velocity" of particle
c1(i) = dsqrt(eightkb*temp/(xpirhop*v1(i))

Particle Knudsen number
x11(i) = 8.0d0*dif1(i)/(vpi*c1(i))
g1(i) = ((x1(i) + x11(i))**3.d0
2 - (x1(i)*x1(i) + x11(i)*x11(i))**1.5d0
2/(3.0d0*x1(i)*x11(i)) - x1(i)
Average ion-properties

ion mobility (m²/V/s)
zion=zaionr*(temp/300.d0)

ion diffusivity (m²/s)
xdIF=rkb*temp*zion/xel

ion mean thermal velocity (m/s)
xicIF=dsqrt(8.d0*rkb*temp/vpi/(xwaion/avog))

ion mean free path (m)
xliP=1.329d0*zion/xel*dsqrt(rkb*temp*xmwg/1000.d0*xwaion/avog)

Knudsen number based on ions
xknIP(i)=2.d0*xliP/x1(i)

Electrostatic dispersion and migration variables

slip correction factor (Hinds, 1999; equation 3.20)
using the collision diameter
ccP(i)=1.d0+xlm/x1(i)*(2.34d0 +1.05d0*dexp(-0.39d0*x1(i)/xlm))

particle mechanical mobility (using the collision diameter)
(Hinds, 1999; equations 3.16, 3.18)
bbP(i)=ccP(i)/3.d0/vpi/eta/x1(i)

terminal electrostatic velocity (m/s) (Hinds, 1999)
xvteP(i)=y(int3num+i)*xel*xfie*bbP(i)

Re number for stokes regime should be < 1 !
xrenP(i)=x1(i)*xvteP(i)/xnu

ELSE
xdpr1(i)  = 0.0d0
xnpr1(i)  = 0.0d0
x1(i)     = 0.0d0
xsurf1(i) = 0.0d0
g1(i)     = 0.0d0
c1(i)     = 0.0d0
dif1(i)   = 0.0d0
xknIP(i)  = 0.0d0
bbP(i)    = 0.0d0
ccP(i)    = 0.0d0
xvteP(i)  = 0.0d0
xrenP(i)  = 0.0d0
ENDIF

Dispersion summation (modifying Vemury et al., 1997; pp 601)
sumdisp = sumdisp + y(int3num+i)*y(i)
END DO
DO i = 1, isec
DO j = 1, i
IF (x1(i).LE.0.d0.AND.x1(j).LE.0.d0) THEN
betafu(i,j)=0.0d0
ELSE

Combination parameters
c12(i,j) = dsqrt(c1(i)**2.d0+c1(j)**2.d0)
g12(i,j) = dsqrt(g1(i)**2.d0+g1(j)**2.d0)
c Fuchs coagulation kernel
betafu(i,j) = (x1(i)+x1(j))/(x1(i)+x1(j)+2.d0*g12(i,j))
betafu(i,j) = betafu(i,j) + 8.d0*(dif1(i)+dif1(j))
  2 /c12(i,j)*(x1(i)+x1(j)))
betafu(i,j) = twopi*(dif1(i)+dif1(j))*(x1(i)+x1(j))
  2 /betafu(i,j)
IF (t.GT.1.d-3.AND.t.LT.xplahe) THEN
  c IF (t.LT.xplahe) THEN
  c Unipolar charging effect (Matsoukas, 1997)
  c Correction of collision kernel for charged particles
  c (Matsoukas, 1997) for the free molecule regime
  c using the aggregate area equivalent diameter
  c xf12P=xel*xel*y(int3num+i)*y(int3num+j)
  c * / (2.d0*vpi*xeo*(xsurf1(i)+xsurf1(j)))
  c using the aggregate collision diameter
  c xf12P=xel*xel*y(int3num+i)*y(int3num+j)
  c * / (2.d0*vpi*xeo*(x1(i)+x1(j)))
  c For repulsion
  xgam12P=dexp(-xf12P/rkb/temp)
ELSE
  c Bipolar charging effect (Matsoukas, 1997)
  xgam12P=1.02d0
END IF
betafu(i,j)=betafu(i,j)*xgam12P
ENDIF
betafu(j,i)=betafu(i,j)
END DO
END DO
c Recalculation of (j,k) aggregation classes
IF (x(2).GE.(x(1)+x(1))) THEN
  jmin(1,1) = 1
  jmax(1,1) = 1
ELSE
  jmin(1,1) = 1
  jmax(1,1) = 0
END IF
DO i = 2,isec-1
  DO k = 1,i
    j = k
    xtmp = x(i-1) - x(k)
    DO WHILE(xtmp.GT.x(j))
      j = j + 1
    END DO
    jmin(i,k) = j
    j = i
    xtmp = x(i+1) - x(k)
    DO WHILE(x(j).GT.xtmp.AND.(j.GE.k))
      j = j - 1
    END DO
    jmax(i,k) = j
  END DO
END DO
DO k = 1,isec
  j = k
  xtmp = x(isec-1) - x(k)
  DO WHILE(xtmp.GT.x(j))
    j = j + 1
  END DO
  jmin(isec,k) = j
jmax(isec,k) = isec
END DO

Growth derivatives
Total particle area in m^2/Kgr-gas
area = 0.0d0
DO i = 1,isec
  area = area + y(i+int2num)
END DO

IF (xk.GT.(xks*area*rhog)) THEN
  xkg=xk-xks*area*rhog
ELSE
  xkg=0.d0
  xks=xk/area/rhog
END IF

DO i = 1,isec
  dNi/dx(surf.)
dyg(i)=0.d0
dx(i)/dx(surf.)
dyg(i+intnum)=xks*conc*avog*rhog*v0*xnpr1(i)**(vpi*xdpr1(i)**2.d0)*xnpr1(i)/vel
END DO

Nucleation derivatives
dyn  = avog*conc*xkg/vel
dynx = dyn*(v0-y(intnum+1))/y(1)

Aggregation derivatives
Birth term
DO i = 1,isec
  suNb = 0.d0
  suAb = 0.d0
  DO k = 1,i
    IF (jmax(i,k).GE.jmin(i,k)) THEN
      DO j = jmin(i,k), jmax(i,k)
        suNb=suNb+halfdel(j,k)*betafu(j,k)*y(j)*y(k)*eeta(x(j)+x(k),i)
        suAb=suAb+halfdel(j,k)*betafu(j,k)*(y(k)*y(j+int2num) + y(j)*y(k+int2num))*y(k)*y(j+int2num)
      END DO
    END IF
  END DO
  dyca(i) = suNb*rhog/vel
  dyca(i+intnum) = 0.d0
  dyca(i+int2num)=suAb*rhog/vel
END DO

Alternative detailed calculation of the aggregation birth terms
applicable when the spacing factor between the first two sections is bigger equal to two
xmax=x(isec)*s
xz=0.d0
xv=1.d0
DO i = 2,isec
  suNb = 0.d0
  suAb = 0.d0
DO k = 1, isec
DO j = 1, k
ww(k,j)=x(j)+x(k)
IF (i.LT.isec) THEN
IF (ww(k,j).GE.x(i-1).AND.ww(k,j).LE.x(i+1)) THEN
xita = (((ww(k,j)**xz)*(x(i+1)**xv)-(ww(k,j)**xv)*(x(i+1)**xz))
*(x(i)**xz)*(x(i+1)**xv)-(x(i)**xv)*(x(i+1)**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(x(i+1)**xv)-(ww(k,j)**(xv-1.d0))
*(x(i)**xz))/(x(i)**(xz-1.d0))*(x(i+1)**xv)
*-(x(i)**(xv-1.d0))*(x(i+1)**xz))
ELSE
xita = (((ww(k,j)**xz)*(x(i-1)**xv)-(ww(k,j)**xv)*(x(i-1)**xz))
*+(x(i)**xz)*(x(i-1)**xv)-(x(i)**xv)*(x(i-1)**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(x(i-1)**xv)-(ww(k,j)**(xv-1.d0))
*(x(i-1)**xz))/(x(i-1)**(xz-1.d0))*(x(i)**xv)
*-(x(i-1)**(xv-1.d0))*(x(i)**xz))
END IF
ELSE
xita = (((ww(k,j)**xz)*(x(i-1)**xv)-(ww(k,j)**xv)*(x(i-1)**xz))
*+(x(i)**xz)*(x(i-1)**xv)-(x(i)**xv)*(x(i-1)**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(x(i-1)**xv)-(ww(k,j)**(xv-1.d0))
*(x(i-1)**xz))/(x(i-1)**(xz-1.d0))*(x(i)**xv)
*-(x(i-1)**(xv-1.d0))*(x(i-1)**xz))
END IF
ENDIF
ENDIF
ELSE
delta=1.d0
ENDIF
suNb=suNb+delta*betafu(j,k)*y(j)*y(k)*xita
suAb=suAb+delta*betafu(j,k)
*+(y(j+int2num)*y(j)+y(j+int2num)*y(k))*xitaV
ENDIF
ENDIF
ELSE
IF (ww(k,j).GE.x(isec-1).AND.ww(k,j).LE.xmax) THEN
xita = (((ww(k,j)**xz)*(xmax**xv)-(ww(k,j)**xv)*(xmax**xz))
*+(x(isec)**xz)*(xmax**xv)-(x(isec)**xv)*(xmax**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(xmax**xv)-(ww(k,j)**(xv-1.d0))
*(x(isec)**xz))/(x(isec)**(xz-1.d0))*(xmax**xv)
*-(x(isec)**(xv-1.d0))*(xmax**xz))
ELSE
xita = (((ww(k,j)**xz)*(x(isec-1)**xv)-(ww(k,j)**xv)*(x(isec-1)**xz))
*-(ww(k,j)**xz)*(x(isec-1)**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(x(isec-1)**xv)-(ww(k,j)**(xv-1.d0))
*(x(isec-1)**xz))
*-(ww(k,j)**(xv-1.d0))*(x(isec-1)**xz))
xita = (((ww(k,j)**xz)*(x(isec-1)**xv)-(ww(k,j)**xv)*(x(isec-1)**xz))
*-(ww(k,j)**xz)*(x(isec-1)**xz))
xitaV = (((ww(k,j)**(xz-1.d0))*(x(isec-1)**xv)-(ww(k,j)**(xv-1.d0))
*(x(isec-1)**xz))
*-(ww(k,j)**(xv-1.d0))*(x(isec-1)**xz))
ENDIF
ELSE
delta=0.5d0
ENDIF
ELSE
delta=1.d0
ENDIF
suNb=suNb+delta*betafu(j,k)*y(j)*y(k)*xita
suAb=suAb+delta*betafu(j,k)
*+(y(j+int2num)*y(j)+y(j+int2num)*y(k))*xitaV
ENDIF
ENDIF
ENDIF
ELSE
IF (j.EQ.k) THEN
delta=0.5d0
ELSE
delta=1.d0
ENDIF
suNb=suNb+delta*betafu(j,k)*y(j)*y(k)*xita
suAb=suAb+delta*betafu(j,k)
*+(y(j+int2num)*y(j)+y(j+int2num)*y(k))*xitaV
ENDIF
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c  Death term
DO  i = 1,isec
  suNd = 0.d0
  suAd = 0.d0
DO  k = 1,isec
  suNd = suNd + betafu(i,k)*y(k)*y(i)
  suAd = suAd + betafu(i,k)*y(k)*y(i+int2num)
END DO
  dycb(i) = suNd*rhog/vel
  dycb(i+intnum) = 0.d0
  dycb(i+int2num)=suAd*rhog/vel
END DO

c  TOTAL DERIVATIVES

  c THIS IS CALLED IF-ELECTRIC
  IF (t.GT.1.d-3.AND.t.LT.xplahe) THEN
    yp(1+intnum)=0.0d0
    *   +dyg(1+intnum)+dynx
  c This is the (sint-if)
  IF ((y(1)*y(1+int2num)).GT.0.0d0) THEN
    d2(1)=xdpr1(1)
    xparam1=1.d0
    c Sintering time by Kobata-(1991)
    c as quoted by Xiong-(1993), in sec
    ts(1)=7.4d8*temp*((d2(1)*100.d0)**4.d0)*dexp(31000.d0/temp)
    xsint(1)=xparam1*(1.d0/ts(1))
    *  *(y(1+intnum)-vpi*((6.d0/vpi*y(1+intnum))**twothirds)*y(1))
  c End of (sint-if)
  ELSE
    xsint(1)=0.d0
  ENDIF
  c FOR THE N1
  yp(1)=0.0d0
    *   +dyca(1)
    *  -dycb(1)+dyn
    c Electrostatic dispersion
    *  -xel*xel/xeo*bbP(1)*y(1)*y(int3num+1)
    *  +sumdisp*rhog/vel
    c Electrostatic migration
    *  -y(1)*xvteP(1)/xwidth/vel
  c FOR THE A1
  yp(1+int2num)=0.0d0
    *   +dyca(1+int2num)
    *  -dycb(1+int2num)+dyn*a0
    *  +dyg(1+int2num)
    *  -xsint(1)/vel
    c Electrostatic dispersion
    *  -xel*xel/xeo*bbP(1)*y(int2num+1)*y(int3num+1)
    *  +sumdisp*rhog/vel
    c Electrostatic migration
    *  -y(int2num+1)*xvteP(1)/xwidth/vel
  c Diffusion and field charging (Lawless, 1996)
  c particle radius (m) used in the charging rate
  c using the primary particle radius
  c xaP(1)=xdpr1(1)/2.d0
using the aggregate area equivalent radius

cxaP(1) = xsurf(1)/2.d0

c using the aggregate collision radius

cxaP(1) = x1(1)/2.d0

c dimensionless electric field

cxwP(1) = xaP(1)*xfie/(rkb*temp/xel)

c dimensionless charge

cxvP(1) = y(int3num+1)*xel*xel/4.d0/vpi/xeo/xaP(1)/rkb/temp

c dimensionless field term

cxfvwP(1) = xdiel*xwP(1)/4.d0*(1.d0-xvP(1)/(xdiel*xwP(1)))*x2.d0

c dimensionless area fraction

if (xwP(1).ge.0.525d0) then
    xfwP(1) = 1.d0/(xwP(1)+0.475d0)**0.575d0
else
    xfwP(1) = 1.d0
endif

c effective knudsen number (assuming sticking probability of 1)
cxeffP(1) = xciP*xkniiP(1)/3.d0/(zpion*xfie)

c dimensionless diffusuion term for uncharged particles

cxbeoP(1) = 1.d0/(1.d0+xeffP(1))

c dimensionless diffusion term for v>+#w

cxbe2P(1) = (xvP(1)-xdiel*xwP(1))/(dexp(xvP(1)-xdiel*xwP(1))-1.d0)
    * xeffP(1)*dexp(xvP(1)-xdiel*xwP(1))

c dimensionless diffusion term for v<-#w

cxbe3P(1) = (-xvP(1)-xdiel*xwP(1))
    / (dexp(-xvP(1)-xdiel*xwP(1))-1.d0)
    * xeffP(1)*dexp(-xvP(1)-xdiel*xwP(1))

c dimensionless rate for several conditions

if ((xvP(1).ge.0.525d0) then
    DCharP(1) = xfwP(1)*xbeoP(1)
else if ((xvP(1).lt.(xdiel*xwP(1))) then
    DCharP(1) = xfwP(1)*xbe3P(1)
endif

FOR THE q1

yp(1+int3num)=0.d0
    * DCharP(1)*(4.d0*vpi*xaP(1)*rkb*temp*xion*rhog/zpion/xel)/vel

For Ni, xi, Ai, qi
DO i = 2,isec

FOR THE Ni

yp(i)=0.d0
    * dyca(i)-dycb(i)

Electrostatic dispersion
    * -xel*xel/xeo*bpi(i)*y(i)*y(int3num+i)
    * sumdisp*rhog/vel

Electrostatic migration
    * -y(i)*xvteP(i)/xwidth/vel

FOR THE xi

yp(i+intnum)=0.d0
* +dyg(i+intnum)
  
c  This is the (sint-if)
  IF ((y(i)*y(i+int2num)).GT.0.0d0) THEN
  
c  SINTERING TERM:
  c  1/tsi(Ai-Ni*asi) in m2/s/Kg
  d2(i)=xdpr1(i)
  xparam=1.d0
  
c  Sintering time by Kobata-(1991)
  c  as quoted by Xiong-(1993), in sec
  ts(i)=7.4d8*temp*((d2(i)*100.d0)**4.d0)*dexp(31000.d0/temp)
  xsint(i)=xparam*(1.d0/ts(i))
  * *(y(i+int2num)-vpi*((6.d0/vpi*y(i+intnum))**twothirds)*y(i))
  
c  End of (sint-if)
  ELSE
  xsint(i)=0.d0
  ENDIF
  
c  FOR THE Ai
  yp(i+int2num)=0.0d0
  * +dyca(i+int2num)-dycb(i+int2num)
  * -xsint(i)/vel
  * +dyg(i+int2num)
  
c  Electrostatic dispersion
  * -xel*xel/xeo*bbP(i)*y(int2num+i)*y(int3num+i)
  * *sumdisp*rhog/vel
  
c  Electrostatic migration
  * -y(int2num+i)*xvteP(i)/xwidth/vel
  
c  Diffusion and field charging (Lawless, 1996)
  
c  particle radius (m) used in the charging rate
  c  using the primary particle radius
  c  xaP(i)=xdpr1(i)/2.d0
  c  using the aggregate area equivalent radius
  c  xaP(i)=xsurf(i)/2.d0
  c  using the aggregate collision radius
  c  xaP(i)=x1(i)/2.d0
  
c  dimensionless electric field
  xwp(i)=xaP(i)*xfie/(rkb*temp/xel)
  
c  dimensionless charge
  xvP(i)=y(int3num+i)*xel*xel/4.d0/vpi/xeo/xaP(i)/rkb/temp
  
c  dimensionless field term
  xfwP(i)=xdiel*xwp(i)/4.d0*(1.d0-xwp(i)/(xdiel*xwp(i)))**2.d0
  
c  dimensionless area fraction
  if (xwp(i).ge.0.525d0) then
  xfwP(i)=1.d0/(xwp(i)+0.475d0)**0.575d0
  else
  xfwP(i)=1.d0
  endif
  
c  effective knudsen number (assuming sticking probability of 1)
  xeffP(i)= xcP*xknif(i)/3.d0/(zpion*xfie)
  
c  dimensionless diffusion term for uncharged particles
xbeoP(i)=1.d0/(1.d0+xeffP(i))
c dimensionless diffusion term for v>+w
xbe2P(i)=(xvP(i)-xdiel*xwP(i))/(dexp(xvP(i)-xdiel*xwP(i))-1.d0
* +xeffP(i)*((xvP(i)-xdiel*xwP(i)))*dexp(xvP(i)-xdiel*xwP(i)))
c dimensionless diffusion term for v<-w
xbe3P(i)=(-xvP(i)-xdiel*xwP(i))
* /(dexp(-xvP(i)-xdiel*xwP(i))-1.d0
* +xeffP(i)*(-xvP(i)-xdiel*xwP(i))*dexp(-xvP(i)-xdiel*xwP(i)))
c dimensionless rate for several conditions
if (xvP(i).ge.(-xdiel*xwP(i)).
* and.xvP(i).le.(xdiel*xwP(i))) then
DFcharP(i)=xfwP(i)+xfP(i)*xbeoP(i)
elseif (xvP(i).gt.(xdiel*xwP(i))) then
DFcharP(i)=xfwP(i)*xbe2P(i)
elseif (xvP(i).lt.(-xdiel*xwP(i))) then
DFcharP(i)=-xvP(i)+xfwP(i)*xbe3P(i)
endif
c FOR THE qi
yp(i+int3num)=0.d0
* +DFcharP(i)*(4.d0*vpi*xaP(i)*rkb*temp*xion*rhog*zpion/xel)/vel
END DO
c THIS IS FOR THE IF-ELECTRIC
ELSE
c FOR THE x1
yp(1+intnum)=0.0d0
* +dyg(1+intnum)+dynx
c This is the (sint-if)
IF ((y(1)*y(1+int2num)).GT.0.0d0) THEN
d2(1)=xdpr1(1)
xparam1=1.d0
ENDIF
c Sintering time by Kobata-(1991)
c as quoted by Xiong-(1993), in sec
ts(1)=7.4d8*temp*((d2(1)*100.0d0)**4.0d0)*dexp(31000.0d0/temp)
xsint(1)=xparam1*(1.d0/ts(1))
* *(y(1+int2num)-vpi*{(6.0d0/vpi*y(1+intnum))**twothirds)*y(1))
c End of (sint-if)
ELSE
xsint(1)=0.d0
ENDIF
c FOR THE N1, A1
c FOR THE N1
yp(1)=0.0d0
* -dycb(1)+dyn
c FOR THE A1
yp(1+int2num)=0.0d0
* -dycb(1+int2num)+dyn*a0
* +dyg(1+int2num)
* -xsint(1)/vel
c FOR THE q1
yp(1+int3num)=0.d0

c For Ni, xi, Ai, qi
DO i = 2,isec

c FOR THE Ni
yp(i)=0.d0
* +dyca(i)-dycb(i)

c FOR THE xi
yp(i+intnum)=0.d0
* +dyg(i+intnum)

c This is the (sint-if)
IF ((y(i)*y(i+int2num)).GT.0.0d0) THEN

c SINTERING TERM:
c 1/tdi(Ai-Ni*asi) in m2/s/Kg
d2(i)=xdpr1(i)
  xparam=1.d0

c Sintering time by Kobata-(1991)
c as quoted by Xiong-(1993), in sec
ts(i)=7.4d8*temp*((d2(i)*100.d0)**4.d0)*dexp(31000.d0/temp)
xsint(i)=xparam*(1.d0/ts(i))
  * *(y(i+int2num)-vpi*((6.d0/vpi*y(i+intnum))**(twothirds))*y(i))

c End of (sint-if)
ELSE
xsint(i)=0.d0
ENDIF

c FOR THE Ai
yp(i+int2num)=0.0d0
* +dyca(i+int2num)-dycb(i+int2num)
* -xsint(i)/vel
* +dyg(i+int2num)

c FOR THE qi
yp(i+int3num)=0.d0
END DO

cthis is for the if-electric
END IF

C For the precursor dC/dx in moles/Kg/m
yp(int4num+1)=0.0d0
* -xk*y(int4num+1)/vel

C Remaining differential equations
DO i = isec+1,intnum
  yp(i) = 0.d0
  yp(i+intnum) = 0.d0
  yp(i+int2num) = 0.d0
  yp(i+int3num) = 0.d0
END DO

RETURN
END
c Calculate Temperature and Velocity

subroutine tempvel(t)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube

tt=t*100.d0

if(tt.lt.0.3d0) then
  temp=((2471.9032d0-400.d0)/0.3d0)*tt+400.d0
else
  ua=2470.2994d0
  ub=-282.9708d0
  uc=19.185d0
  ud=-0.1228d0
  ue=0.0282d0
  temp=(ua+ub*tt+uc*tt**2.d0)
  /(1.d0+ud*tt+ue*tt**2.d0)
endif

c VELOCITY PROFILE (m/s)

c Reference temperature (K)
tref=298.15d0

c Total inlet flow-rate (m3/s)
xqtot=6.55d0/1000.d0/60.d0

c Velocity (m/s) (Pressure=const=1 atm)
vel=4.d0*xqtot/(vpi*xdtube**2.d0)*temp/tref

return
end

c Calculate physical properties of gas

subroutine props
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/visc/sigmavis,epsovk,xa1,xb2,xc3,xd4,xe5,xf6

c Calculate gas viscosity, density, and mean free path

c (Reid, Prausnitz, and Poling, 1988) omegav
c (Bird, Stewart, and Lightfoot, 1960) eta
c (Friedlander, 1977) xlm

tstar=temp/epsovk
omegav=xa1/tstar**xb2+xc3/dexp(xd4*tstar)+xe5/dexp(xf6*tstar)

c Gas Density in Kg/m3
rhog=p*xmwg/rgas/temp

c Gas viscosity in kg/s/m
eta=(2.6693d-26)*dsqrt(xmwg*temp)/omegav/(sigmavis**2.d0)

c Gas kinematic viscosity in m2/s
xnu=eta/rhog

c Gas free mean path in m
xlm = xnu * dsqrt(vpi * xmwg / 2.0 / 8.31441d0 / temp / 1.0d3)

return
end

**Calculate moment #j of the distribution y, aggregates**

double precision function dmoment(y, j)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum), y(int4num+1)
dimension betafu(intnum, intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas8/isec

sum = 0.0d0
DO i = 1,isec
  IF (y(i).GT.0.0d0) THEN
    sum = sum + y(i)*(x(i)**DFLOAT(j))
  END IF
END DO
dmoment = sum
RETURN
END

**Calculate eta coefficient in aggregation birth term**

c the function is called eeta because of real eta variable
c here used for the number concentrations

double precision function eeta(w, i)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum), y(int4num+1)
dimension betafu(intnum, intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas8/isec

IF (w.LE.x(isec)) THEN
  IF (w.GE.x(i)) THEN
    eeta = (x(i+1)-w)/(x(i+1)-x(i))
  ELSE
    eeta = (x(i-1)-w)/(x(i-1)-x(i))
  END IF
ELSE
  eeta = 1.0d0
ENDIF
RETURN
END
Calculate eta coefficient in area aggregation birth term

the function is called eetaV because of real eta variable
here used for the area concentrations
double precision function eetaV(w,i)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum), y(int4num+1)
dimension betafu(intnum,intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas8/isec

IF (w.LE.x(isec)) THEN
IF (w.GE.x(i)) THEN
c  Eeta is: non-dimensional case
eetaV = (x(i+1)/w-1.d0)/(x(i+1)/x(i)-1.d0)
ELSE
c  Eeta is: non-dimensional case
eetaV = (x(i-1)/w-1.d0)/(x(i-1)/x(i)-1.d0)
END IF
ELSE
c  For eeta = 1 => w = x(i) thus also eetaV = 1
eetaV = 1.d0
END IF
RETURN
END

Simple function for aggregation
double precision function halfdel(j,k)
implicit real*8(a-h,n-z)
implicit integer*4 (i-m)

IF (j.EQ.k) THEN
halfdel = 0.5d0
ELSE
halfdel = 1.d0
END IF
RETURN
END

Grid transformation

SUBROUTINE regrid(y)
implicit real*8 (a-h,n-z)
implicit integer*4 (i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension y(int4num+1)
dimension x(intnum),betafu(intnum,intnum)
dimension jmin(intnum,intnum+1),jmax(intnum,intnum+1)
dimension v(intnum+1)
dimension xnew(intnum), ynew(int4num+1)
common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas5/a,b,c,d
common/bas6/jmin, jmax
common/bas7/v
common/bas8/isec
common/bas9/d0
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg
external vodpk

C Initialization of new grid points and populations
DO i = 1,intnum
   ynew(i) = 0.0d0
   ynew(i+intnum) = 0.0d0
   ynew(i+int2num) = 0.0d0
   ynew(i+int3num) = 0.0d0
   xnew(i) = 0.0d0
   x(i) = y(i+intnum)
END DO

ynew(int4num+1)=0.0d0
popmin = 1.d-27
precmin = 1.d-1
C Add a new section
xnew(1) = v0
ynew(1+intnum) = xnew(1)
ynew(1) = 1.d0
ynew(1+int2num) = ynew(1)*a0
ynew(1+int3num) = 0.0d0
DO i = 2,isec+1
   xnew(i) = x(i-1)
ynew(i) = y(i-1)
ynew(intnum+i) = xnew(i)
ynew(int2num+i) = y(int2num+i-1)
ynew(int3num+i) = y(int3num+i-1)
END DO

ynew(int4num+1)=y(int4num+1)
isec = isec+1
C Empty and eliminate grid points
scrit = s**1.1d0
i = 2
DO WHILE (i.LT.(isec-1))
   IF ((xnew(i+1)/xnew(i-1)).LT.scrit) THEN
      C Empty grid point (z=0 and v=1)
adllow = (xnew(i+1)-xnew(i))/(xnew(i+1)-xnew(i-1))
adup = (xnew(i)-xnew(i-1))/(xnew(i+1)-xnew(i-1))
      C For ai not constant (but preserving A(total))
ynew(i-1+int2num) = ynew(i-1+int2num)+adllow*ynew(i+int2num)
ynew(i+1+int2num) = ynew(i+1+int2num)+adup*ynew(i+int2num)
      C Dispose of Ai
      ynew(i+int2num) = 0.0d0
   ELSE
      IF((ynew(i-1)+ynew(i)*adllow).gt.0.d0) then

ynew(i-1+int3num) = (ynew(i-1)*ynew(i-1+int3num) * +addlow*ynew(i)*ynew(i+int3num)) * / (ynew(i-1)+ynew(i)*addlow) 
else 
ynew(i-1+int3num) = 0.d0 
endif 
if((ynew(i+1)+ynew(i)*addup).gt.0.d0) then 
ynew(i+1+int3num) = (ynew(i+1)*ynew(i+1+int3num) * +addup*ynew(i)*ynew(i+int3num)) * / (ynew(i+1)+ynew(i)*addup) 
else 
ynew(i+1+int3num) = 0.d0 
endif 
c Dispose of qi 
ynew(i+int3num) = 0.0d0 
c For Ni splitting preserving both numbers and mass 
ynew(i-1) = ynew(i-1) + ynew(i)*addlow 
ynew(i+1) = ynew(i+1) + ynew(i)*addup 
c Dispose of Ni 
ynew(i) = 0.0d0 
c Eliminate grid point 
DO j = i,isec-1 
ynew(j) = ynew(j+1) 
ynew(j+intnum) = ynew(j+intnum+1) 
xnew(j) = ynew(j+intnum) 
ynew(j+int2num) = ynew(j+int2num+1) 
ynew(j+int3num) = ynew(j+int3num+1) 
END DO 
isec = isec - 1 
END IF 
i = i + 1 
END DO 
c Replacement of old populations and grid points 
DO i = 1,isec 
y(i) = ynew(i) 
y(i+intnum) = xnew(i) 
x(i) = xnew(i) 
y(i+int2num) = ynew(i+int2num) 
y(i+int3num) = ynew(i+int3num) 
END DO 
y(int4num+1)=ynew(int4num+1) 
c Initialization of unused x and y array space 
DO i = isec+1,intnum 
x(i) = 0.d0 
y(intnum+i) = x(i) 
y(i) = 0.d0 
y(i+int2num) = 0.d0 
y(i+int3num) = 0.d0 
END DO 
RETURN 
END 
c Calculate primary particle total number concentration 

double precision function xntotp(y) 
implicit real*8(a-h,n-z) 
implicit integer*4(i-m) 
parameter (intnum = 70) 
parameter (int2num = 2*intnum) 
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum),y(int4num+1)
dimension betafu(intnum,intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas8/isec

sum=0.d0
DO i=1, isec
IF ((y(i)*y(i+int2num)).GT.0.d0) THEN
x(i)=y(i+intnum)
sum=sum+y(i)*((y(int2num+i)/y(i))**3.d0)/36.d0/vpi/x(i)/x(i)
END IF
END DO
xntotp=sum
RETURN
END

c Calculate number based standard geometric deviation
c of the distribution of the primaries
c n(v,t) is written as a sum of deltas (Kumar & Ramkrishna)

double precision function sigmagkrp(y,t)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum),y(int4num+1)
dimension betafu(intnum,intnum),v(intnum+1)
dimension tnprim(intnum)
common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas7/v
common/bas8/isec
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg

xlnvgp=0.d0
DO k = 1,isec
IF ((y(k)**(y(int2num+k))).GT.0.d0) THEN
  tnprim(k)=((y(int2num+k)/y(k))**3.d0)/36.d0/vpi/x(k)/x(k)
  xlnvgp=xlnvgp+y(k)*tnprim(k)*DLOG(x(k)/tnprim(k))/xntotp(y)
END IF
END DO
vgp = DEXP(xlnvgp)

xln2sgp = 0.0d0
DO k = 1,isec
IF ((y(k)**(y(int2num+k))).GT.0.d0) THEN
  xln2sgp=xln2sgp+y(k)*tnprim(k)*DLOG(x(k)/tnprim(k)/vgp)
  * DLOG(x(k)/tnprim(k)/vgp)/xntotp(y)/9.d0
END IF
END DO

sigmagkrp=DEXP(DSQRT(xln2sgp))

RETURN
END
Calculate volume based standard geometric deviation of the distribution of the primaries

\[ n(v, t) \text{ is written as a sum of deltas (Kumar & Ramkrishna)} \]

double precision function sigmagvkrp(y, t)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
dimension x(intnum), y(int4num+1)
dimension betafu(intnum,intnum), v(intnum+1)
dimension snprim(intnum)

common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas7/v
common/bas8/isec
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg

c Total volume of primaries = total volume of aggregates
xvtotal = dmoment(y,1)
xlnvgp = 0.d0
DO k = 1,isec
IF ((y(k)*y(int2num+k)).GT.0.d0) THEN
snprim(k)=(((y(int2num+k)/y(k))**3.d0)/36.d0/vpi/x(k)/x(k))
xlnvgp=xlnvgp+x(k)*y(k)*DLOG(x(k)/snprim(k))/xvtotal
END IF
END DO
vgp = DEXP(xlnvgp)
xln2sgp = 0.0d0
DO k = 1,isec
IF ((y(k)*y(int2num+k)).GT.0.d0) THEN
xln2sgp=xln2sgp+x(k)*y(k)*DLOG(x(k)/snprim(k)/vgp)
* *DLOG(x(k)/snprim(k)/vgp)/9.d0/xvtotal
END IF
END DO
sigmagvkrp = DEXP(DSQRT(xln2sgp))

RETURN
END

Calculate number based standard geometric deviation of the distribution of the aggregates (i starting from 1)

\[ n(v, t) \text{ is written as a sum of deltas (Kumar & Ramkrishna)} \]

double precision function sigmagkra1(y, t)
implicit real*8(a-h,n-z)
implicit integer*4(i-m)
parameter (intnum = 70)
parameter (int2num = 2*intnum)
parameter (int3num = 3*intnum)
parameter (int4num = 4*intnum)
common/bas1/c0,v0,a0,vpi,rkb,avog,rgas,p,temp,vel,xdtube
common/bas2/xmwg,rhog,rhop,xnu,eta,xlm,conc,xdf
common/bas3/s,xshnum,xsharea,xshvol
common/bas4/x,betafu,dynx
common/bas7/v
common/bas8/isec
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg

DO k = 1,isec
IF ((y(k)*y(int2num+k)).GT.0.d0) THEN
snprim(k)=(((y(int2num+k)/y(k))**3.d0)/36.d0/vpi/x(k)/x(k))
xlnvgp=xlnvgp+x(k)*y(k)*DLOG(x(k)/snprim(k))/xvtotal
END IF
END DO
vgp = DEXP(xlnvgp)
xln2sgp = 0.0d0
DO k = 1,isec
IF ((y(k)*y(int2num+k)).GT.0.d0) THEN
xln2sgp=xln2sgp+x(k)*y(k)*DLOG(x(k)/snprim(k)/vgp)
* *DLOG(x(k)/snprim(k)/vgp)/9.d0/xvtotal
END IF
END DO
sigmagkra1 = DEXP(DSQRT(xln2sgp))

RETURN
END
common/bas8/isecl
common/kinetic/gaspre,gase,surfpre,surfe,xk,xks,xkg
common/geometric1/vga1,dvga1

dimension x(intnum),y(int4num+1)
dimension betafu(intnum,intnum),v(intnum+1)
dimension tnprim(intnum)

xtotag1=0.0d0
DO k=1, isec
  xtotag1=xtotag1+y(k)
END DO

xlnvga1=0.d0
DO k = 1,isec
  xlnvga1=xlnvga1+y(k)*DLOG(x(k))/xtotag1
END DO

vga1 = DEXP(xlnvga1)
dvga1 = (6.d0/vpi*vga1)**(1.d0/3.d0)
xln2sga1 = 0.0d0

DO k = 1,isec
  xln2sga1=xln2sga1+y(k)*DLOG(x(k)/vga1)/xtotag1/9.d0
END DO

sigmagkra1=DEXP(DSQRT(xln2sga1))
RETURN
END

**SOLVER**

SUBROUTINE VODPK (F,NEQ,Y,T,TOUT,ITOL,RTOL,ATOL,ITASK,1  ISTATE,IOPT,RWORK,LRW,IWORK,LIW,JAC,PSOL,MF,RPAR,IPAR)
EXTERNAL F, JAC, PSOL
DOUBLE PRECISION Y,T,TOUT,ITOL,RTOL,ATOL,ITASK,1  ISTATE,IOPT,LW,LIW,JAC,PSOL,RFAR,IPAR
INTEGER NEQ,ITOL,ITASK,ISTATE,IOPT,LRW,LIW,MF,IPAR
DIMENSION Y(*),RTOL(*),ATOL(*),RWORK(LRW),IWORK(LIW),1  RFAR(*), IPAR(*)
APPENDIX I

I.1. Fixed sectional code for coagulation and sintering

c   CGS units unless otherwise stated

Program krustav

implicit double precision(a-h,o-z)
parameter(max=50,mmax=100,mmmax=150)
dimension y(mmmax+2),iwk(10000),wk(10000)
dimension v(max+1),ds(max+1),dsa(max),dln(max)
dimension xxl(max+40),yyi(max+40),d(max),vre(max)
dimension xnpnl(max),dsb(max),dsc(max),vp(max+1)
dimension dpml(max+1),vpml(max+1),vl(max+1)
dimension ynpn(max),ynp2n(max),yvol(max),yvoll(max)
dimension xdpnl(max),xnpnl(max),xnpnl(max),xdlog(max)
dimension xlnnd(max),vban(max+1),vbs(max),znprl(max)

external fcn,fcnj

common/block1/xav,xkb,xpi,xsigma,xekb,r
common/block2/xno,xvo,xao,xd,xm,vel
common/block3/x1,x2,x3,x4,x5,x6
common/block4/xmwp,xrhog,xmwp,p
common/block5/xrhog,tstex,omega
common/block6/xmwp,xrhog,tsx,tmx,znprl
common/block7/xc(max+1),xlag(max+1)
common/block8/xs(max+1),ts(max+1)
common/block9/xdf(max),xmome2,xmome3
common/block10/beta(max+1),dmome3
common/block11/d2(max+1),d2max(max+1)

c   gas properties: H2

data xav,xkb,xpi,r/6.022137d23,1.38066d-16
*      ,3.1415926536d0,0.082d0/
data xmwp,xrhog,xsigma,xekb/28.086d0,2.33d0,2.827d-10,59.7d0/
data x1,x2,x3,x4,x5,x6,xmwp,xm,tem,vel
*     ,1.16145d0,0.14874d0,0.52487d0,2.d0,1.0d0/
c   Constant Temperature, K
tem=1073.d0

c   Si Concentration in molecules/cm3
xno=3.6212d21/tem

c   monomer diameter, volume and area
xd=3.3689d-8
xvo=xpi/6.0d0*xdo**3.0d0
xao=xpi*xdo**2.0d0

c   Initial Values

c   Number and Area concentrations
y(1)=xno
y(max+1)=xno*xao
dimension
y(i)=1.0d-30
y(max+i)=xao*1.0d-30

c   mass fractal dimension
xdf(iz)=1.8d0
43 continue

c Volume Concentrations, here as dummy arguments
y(mmax+1)=1.d0
do 431 iy=2, max
y(mmax+iy)=1.d0
431 continue

c Dummy argument for the mmax+1 element
y(mmax+1)=0.0d0

c Reaction input
c For Instant reaction this is dummy argument
y(mmax+2)=0.d0

c Time covered (sec)
rtm=1.d-3

c Dgear Parameters
h     = 1.0d-90
tol   = 1.0d-10
dst   = 4.d3
tim   = 0.d0
h1    = rtm/dst
meth  = 2
miter = 0
index = 1
ier   = 0

c number of equations
n     = mmax+2

c output files
open(unit=11,file='krustav1-a.txt')
10 if (tim.lt.1.d-6) then
tend=tim+1.d-7
elseif (tim.lt.1.d-5.and.tim.ge.1.d-6) then
tend=tim+1.d-6
elseif (tim.lt.1.d-4.and.tim.ge.1.d-5) then
tend=tim+1.d-5
elseif (tim.lt.rtm.and.tim.ge.1.d-4) then
tend=tim+1.d-4
endif

call dgear(n,fcn,fcnj,tim,h,y,tend,tol,meth,miter,index,
1       iwk,wk,ier)

if(ier.gt.128) then
   goto 99
endif

c PostProcessing
xmtot=0.0d0
xmtot2=0.0d0
xstot=0.0d0
xdpri=0.0d0
xnpri=0.0d0
sumdv=0.0d0
totalN=0.0d0
totalV=0.0d0
totalV2=0.0d0
totalmom0=0.0d0
totalmom1=0.0d0
totalmom1b=0.0d0
ysinN=0.0d0
do 440 irr=1, max
c total particle number concentration (#/cm3)
ysinN=ysinN+y(irr)
v(irr)=xvo*(2.0d0**(irr-1))
c total particle volume concentration (cm3/cm3)
xmtot=xmtot+y(irr)*v(irr)*xrhop
xmtot2=xmtot2+y(mmax+irr)*xrhop
xmtot2=xmtot2+y(mmax+irr)*xrhop
c total particle area concentration (cm2/cm3)
xstot=xstot+y(max+irr)
440 continue
c For Aggregates
ytotv=0.0d0
ytotv2=0.0d0
ytotv3=0.0d0
ytotva=0.0d0
ytotvb=0.0d0
sumdv=0.0d0
ytotv2n=0.0d0
ytotv3n=0.0d0
ytotvan=0.0d0
sumdvn=0.0d0
c calculate intermediate parameters for average values
do 990 irv=1, max
if ((y(irv)*y(max+irv)*y(mmax+irv)).gt.0.d0) then
v(irv)=xvo*(2.0d0**(irv-1))
ytotv=ytotv+y(irv)
sumdv=sumdv+y(irv)*(6.0d0*v(irv)/xpi)**(1.0d0/3.0d0)
sumdvn=sumdvn+y(irv)*(6.d0*y(mmax+irv)/y(irv)/xpi)**(1.d0/3.d0)
ytotv2=ytotv2+y(irv)*v(irv)*((6.d0/xpi*v(irv))**(1.d0/3.d0))
ytotv2n=ytotv2n+y(mmax+irv)
*y*(6.d0*y(mmax+irv)/y(irv)/xpi)**(1.d0/3.d0)
ytotv3=ytotv3+y(irv)*v(irv)
ytotv3n=ytotv3+y(mmax+irv)
endif
990 continue
do 881 ivol=1, max
v(ivol)=xvo*(2.0d0**(ivol-1))
ytotva=ytotva+v(ivol)*y(ivol)
ytotvan=ytotvan+y(mmax+ivol)
ytotvb=ytotvb+y(ivol)
881 continue
c Arithmetic Average Volume Equivalent Diameter of Aggregates, nm
dvav=sumdv/ytotv**1.d7
dvavn=sumdvn/ytotv**1.d7
c Volume/mass Aververage Volume

c Equivalent Diameter of Aggregates, nm
Diameter of Average Volume for Aggregates, nm

dvav2 = ((6.0d0/xpi*ytotva/ytotvb)**(1.0d0/3.0d0))*1.d7
dvav2n = ((6.0d0/xpi*ytotvan/ytotvb)**(1.0d0/3.0d0))*1.d7

For Primaries

ytotv6 = 0.0d0
ytotv7 = 0.0d0
ytotv8 = 0.0d0
ytotv9 = 0.0d0
ytotv14 = 0.0d0
xdpri = 0.0d0
xnpri = 0.0d0
ytotmpv = 0.0d0
ytotmpa = 0.0d0
ytotv6n = 0.0d0
ytotv7n = 0.0d0
ytotv8n = 0.0d0
ytotv14n = 0.0d0
xdprin = 0.0d0
xnprin = 0.0d0

calculate intermediate parameters for average values

do 991 irp = 1, max
  if ((y(irp)*y(max+irp)*y(mmax+irp)).gt.0.d0) then
    v(irp) = xvo*(2.0d0**(irp-1))
    xdpri = xdpri + (6.0d0*v(irp)/y(max+irp)*y(irp))
    * (((y(max+irp)/y(irp))**3.d0)/36.d0/xpi/v(irp)
      * v(irp))*y(irp)
  end if
  xdpri = xdpri + (6.0d0*y(mmax+irp)/y(max+irp))
  * (((y(max+irp)/y(irp))**3.d0)/36.d0/xpi/(y(mmax+irp)/y(irp))
  * (y(mmax+irp)/y(irp)))*y(irp)
  xnpri = xnpri + y(irp)*(((y(max+irp)/y(irp))**3.d0)/36.d0/xpi
  * v(irp)/v(irp))
  xnpri = xnpri + y(irp)*(((y(max+irp)/y(irp))**3.d0)/36.d0/xpi
  * (y(mmax+irp)/y(irp))/y(mmax+irp))
  c Reminder: Ni*(ni*vpi)=Ni*vi
  ytotv6 = ytotv6 + (6.0d0*v(irp)/y(max+irp)*y(irp))
  * y(irp)*y(irp)
  ytotv6n = ytotv6n + (6.0d0*y(mmax+irp)/y(max+irp))
  * y(mmax+irp)
  ytotv7 = ytotv7 + v(irp)*y(irp)
  ytotv7n = ytotv7n + y(mmax+irp)
  ytotv8 = ytotv8 + y(irp)*v(irp)
  ytotv8n = ytotv8n + y(mmax+irp)
  ytotv9 = ytotv9 + y(max+irp)
  ytotv14 = ytotv14 + (6.0d0*y(irp)/y(max+irp)*y(irp))**2.d0
  * xpi*(((y(max+irp)/y(irp))**3.d0)/36.d0/xpi/v(irp)
* /v(irp)) * y(irp)

\[ y_{totv14n} = y_{totv14n} + ((6.0 * y(mmax+irp) / y(max+irp))^{2.0}) \]
* xpi*(((y(max+irp)/y(irp))^{3.0})/36.0/xpi
* (y(mmax+irp)/y(irp)))*y(irp)

\[ y_{totmpv} = y_{totmpv} + y(mmax+irp) \]
\[ y_{totmpa} = y_{totmpa} + (y(max+irp)^{3.0})/(y(mmax+irp)^{2.0}) \]
endif

991 continue

c Arithmetic Average primary particle diameter based on Ni*ni, nm
avdprime=xdpri/xnpri*1.d7
avdprimen=xdprin/xnprin*1.d7

c Volume/mass Average primary particle diameter, nm
avdprime3=ytotv6/ytotv7*1.d7
avdprime3n=ytotv6n/ytotv7n*1.d7

c BET Average primary particle diameter, nm
avdprime4=6.0*ytotv8/ytotv9*1.d7
avdprime4n=6.0*ytotv8n/ytotv9*1.d7

c N-Mean area average primary particle diameter, nm
avdprime6=(dsqrt(ytotv14/xnpri/xpi))*1.d7
avdprime6n=(dsqrt(ytotv14n/xnprin/xpi))*1.d7

c Diameter of average mass for the primaries, nm
avdprime7n=(6.0*((ytotmpv/ytotmpa)**(1.0/3.0)))*1.d7

c Average np, based on BET-dp
xnpavbet=(ytotv8/ytotvb)/(xpi/6.0*(avdprime4*1.d-7)**3.0)

c Average np, based on N-dp
xnpavnum=(ytotv8/ytotvb)/(xpi/6.0*(avdprime*1.d-7)**3.0)

c Average np
xnpav=(ytotv9**3.0)/(36.0*xpi*(ytotv8**2.0)*ytotvb)

c Number-Average np
xnpmean=xnpri/ytotvb

c Mass Balance (with instant chemical rxn)
xmass=xno*xvo*xrhop
xmbal=(xmass-xmtot)/xmass*100.d0

c Monitor output values
write(6,100)tend,xmbal,avdprime4
call flush(6)
write(11,100)tend,ytotvb/xno,xnpmean,xnpavbet,xnpavnum,
* avdprime4,avdprime
call flush(11)

if (tim.lt.rtm) goto 10
100 format(7(2x,e11.6))
99 stop
end

c Subroutine FCN
subroutine fcn(n,tim,y,dydt)
parameter(max=50, mmax=100, mmmax=150)
imPLICIT DOUBLE PRECISION(a-h,o-z)
dimension y(mmax+2), dydt(mmax+2)
dimension v(max+1), vv(max+1)
dimension dd2(max+1), dd2max(max+1)
dimension xcc(max, max), xgg(max, max), dc(max)
dimension xkn(max), xg(max), xdiff(max), xsint(max)
dimension zvpr1(max), zdpr1(max), znpr1(max)

common/block1/xav, xkb, xpi, xsigma, xekb, r
common/block2/xno, xvo, xao, xdo, tem, vel
common/block3/x1, x2, x3, x4, x5, x6
common/block4/xmwp, xrhog, xmwg, p
common/block5/xrhog, tstar, omega
common/block6/xmwp, xrhog, tstar, omega
common/block7/xmwp, xrhog, tstar, omega
common/block8/xmwp, xrhog, tstar, omega
common/block9/xmwp, xrhog, tstar, omega
common/block10/xmwp, xrhog, tstar, omega
common/block11/xmwp, xrhog, tstar, omega

vel=1.d0

gas density, g/cm3 (at 1 atm)
% xrhog=1.01325d6*vmwm/8.31451d7/tem

gas viscosity (Chapman Enskog), g/cm/s
tstar=tem/xekb
omega=(x1*tstar**(-x2))
*x3*exp(-x4*tstar)+x5*exp(-x6*tstar)
xmu=(2.6693d-25)*dsqrt(xmwg*tem)/(xsigma*xsigma*omega)

gas free mean path, cm
xlam=xmu*dsqrt(xpi*xmwg/(2.d0*tem*8.314d7))

calculation of collision kernel

%.continue
46 continue

% do 46 il=1, max
% do 47 il2=1, max
beta(il, il2)=0.0d0
%.continue
49 continue

% do 49 is=1, max
v(is)=(2.0d0**(is-1))*xvo
if((y(is)*y(max+is)*y(mmax+is)).gt.0.0d0) then

% Primary particle diameter, cm
zdpr1(is)=6.d0*v(is)*y(is)/y(max+is)

% Primary particle volume, cm3
zvpr1(is)=xpi/6.d0*dzpr1(is)**3.d0
% Number of primaries per aggregate
znpr1(is)=v(is)/zvpr1(is)

% Collision diameter, cm
dc(is)=zdpr1(is)*(znpr1(is))**(1.d0/xdf(is))
aggregate velocity, cm/s
\(v_{\text{is}} = \sqrt{\frac{8 \times x_{\text{kb}} \times \text{tem}}{\pi \times x_{\rho_{\text{hop}}}} / v_{\text{is}}} \)

Knudsen number
\( x_{\text{kn}} \) = 2.0 \times x_{\text{lam}} / dc_{\text{is}}

diffusion coefficient, cm²/s
\( x_{\text{dif}}_{\text{is}} = \frac{x_{\text{kb}} \times \text{tem}}{3.0 \times \pi \times \mu_{\text{is}} / dc_{\text{is}}} \times (5.0+4.0 \times x_{\text{kn}}_{\text{is}}+6.0 \times x_{\text{kn}}_{\text{is}}^2+2.0+18.0 \times x_{\text{kn}}_{\text{is}}^3)/(5.0-x_{\text{kn}}_{\text{is}}+(8.0+\pi) \times x_{\text{kn}}_{\text{is}}^2) \)

aggregate free mean path, cm
\( x_{\text{lag}}_{\text{is}} = 8.0 \times x_{\text{dif}}_{\text{is}} / \pi / x_{\text{c}}_{\text{is}} \)

parameter \( g \)
\( x_{\text{g}}_{\text{is}} = \frac{1.0}{3.0 \times dc_{\text{is}} \times x_{\text{lag}}_{\text{is}}} \times ((dc_{\text{is}}+x_{\text{lag}}_{\text{is}})^3-(dc_{\text{is}}^2+x_{\text{lag}}_{\text{is}}^2)^{3/2})-dc_{\text{is}} \)

else
\( zn_{\text{pr1}}_{\text{is}} = 0.0 \)
\( dc_{\text{is}} = 0.0 \)
\( x_{\text{g}}_{\text{is}} = 0.0 \)
\( x_{\text{c}}_{\text{is}} = 0.0 \)
\( x_{\text{dif}}_{\text{is}} = 0.0 \)
endif

System of Differential Equations
dummy argument for reaction rate and mmmmax+1 point
\( x_{\text{rrt}} = 0.0 \)
\( dydt_{\text{max}+2} = 0.0 \)
\( dydt_{\text{max}+1} = 0.0 \)
do 144 j1=1, max

if (dc(j1).gt.0.0) then

if (dc(j1).le.0.0 and dc(j2).le.0.0) then
\( \beta_{\text{j1,j2}} = 0.0 \)
else
\( x_{\text{gg}}_{\text{j1,j2}} = \sqrt{x_{\text{g}}_{\text{j1}}^2+x_{\text{g}}_{\text{j2}}^2} \)
\( x_{\text{cc}}_{\text{j1,j2}} = \sqrt{x_{\text{c}}_{\text{j1}}^2+x_{\text{c}}_{\text{j2}}^2} \)
\( \beta_{\text{j1,j2}} = 2.0 \times \pi \times (dc_{\text{j1}}+dc_{\text{j2}}) \times (xd_{\text{j1}}+xd_{\text{j2}}) / (((dc_{\text{j1}}+dc_{\text{j2}})/(dc_{\text{j1}}+dc_{\text{j2}}+2.0 \times x_{\text{gg}}_{\text{j1,j2}}))*+(8.0 \times (x_{\text{dif}}_{\text{j1}}+x_{\text{dif}}_{\text{j2}})/(x_{\text{cc}}_{\text{j1,j2}}+x_{\text{cc}}_{\text{j1,j2}}) \times (dc_{\text{j1}}+dc_{\text{j2}}))) \)
endif

51 continue

System of Differential Equations

Dummy argument for reaction rate and mmmmax+1 point
\( x_{\text{rrt}} = 0.0 \)
\( dydt_{\text{max}+2} = 0.0 \)
\( dydt_{\text{max}+1} = 0.0 \)
do 144 j1=1, max

Representative points
\( v_{\text{j1}} = (2.0 \times (j1-1)) \times x_{\text{vo}} \)

This is called surf-if
if (dc(j1).gt.0.0) then
\( d2_{\text{j1}} = 6.0 \times v_{\text{j1}} / y_{\text{j1+max}} \times y_{\text{j1}} \)
d2max(j1)=(6.d0/xpi*v(j1))**(1.d0/3.d0)

c Sintering time of Si particles, Kruis et al., 1993
ts(j)=1.148d13*tem*(dexp(27664.d0/tem))*((d2(j1)*1.d-2)**4.d0)

xparam=1.d0
xsint(j1)=xparam*(1.d0/ts(j1))
* *(y(j1+max)-((v(j1)/xvo)**(2.d0/3.d0))
* *xao*y(j1))

cccc this is for the surf-if
else
xsint(j1)=0.0d0
d2(j1)=0.0d0
endif

c Hounslow et al. (1988) model for coagulation
c FIRST SECTION

if (j1.lt.2) then
  sum1=0.0d0
  do 142 k=1, max
    sum1=sum1+y(k)*beta(1,k)
  142 continue
  dydt(1)=-y(1)*sum1

c Area derivatives
  dydt(max+1)=-y(max+1)*sum1

c dummy argument for volume
  dydt(mmax+1)=0.d0

c SECOND SECTION

elseif (j1.lt.3.and.j1.gt.1) then
  sum2=0.0d0
  do 143 kk=2, max
    sum2=sum2+y(kk)*beta(2,kk)
  143 continue
  dydt(2)=(0.5d0*beta(1,1)*y(1)**2
  * -0.5d0*beta(2,1)*y(2)*y(1)
  * -y(2)**2*sum2)

c Area derivatives
  dydt(max+2)=(beta(1,1)*y(1)*y(max+1)
  * -beta(2,1)*y(2)*y(max+1)
  * -y(max+2)*sum2)
  * -xsint(2)/vel

c dummy argument for volume
  dydt(mmax+2)=0.d0

c SECTIONS FROM 3 to MAX
elseif (j1.gt.2) then
  sum3=0.00d0
  sum4=0.00d0
  sum5=0.00d0
  suma3=0.0d0
  suma4=0.0d0
**Subroutine FCNJ** (Dummy)

```fortran
subroutine fcnj(n,tim,y,pd)
  parameter(max=50, mmax=100, mmmax=150)
  integer n
  double precision tim, y(mmmax+2), pd(mmmax+2,mmmax+2)
  return
end
```

**Solver - DGEAR** (Lahey Fortran & IBM Professional Fortran)
APPENDIX J

J.1. Monodisperse code for gas phase chemical reaction, surface growth, coagulation, sintering and coalescence heat release

c CGS UNITS (unless otherwise stated)

program hen21ssikzks
implicit doubleprecision (a-h, o-z)
dimension y(5),iwk(10000),rwk(10000)
external fcn

common/block1/xno,xpd,xrc,r,p
common/block2/xav,xkb,xpi,vel
common/block3/xmwp,xrhop,xsigma,xekb,xmwg
common/block4/xdf,xnp,xpdm,xcol,xrhog,xsin
common/block5/x1,x2,x3,x4,x5,x6
common/block6/xvo,xdo,xao,tem
common/block7/xrrt,xrrs,xrg
common/block8/ctio2,sbolt,emis,stens

c Gas properties refer to Air

c Reference conditions: standard: 298.15 K, 1 atm

data xav,xkb,xpi/6.022137d23,1.38066d-16,3.1415926d0/
data xmwp,xrhop,xsigma,xekb,xmwg/79.9d0,
* 4.0d0,3.711d-10,78.6d0,28.80d0/
data xdf,r,p/1.8d0,0.082d0,1.d0/
data x1,x2,x3,x4,x5,x6/0.14874d0,0.52487d0,0.77320d0,
* 2.16178d0,2.43787d0/
c TiO2 Specific Heat (assuming: cv=cp) (Holman, 1997; pp 641)
c in cm²*g/sec²/K/#
ctio2=0.7d0*xmwp*1.d7/xav
c Stefan Boltzman constant (Holman, 1997; last page), in g/K⁴/s³
sbolt=5.669d-5
c TiO2 emissivity (Approximation from Holman, 1997; pp 651-652)
c range 0.4-0.9
emis=0.6d0
c TiO2 surface energy (Xing and Rosner, 1999) in g/s²

c for solid-gas: 2.14 J/m²
c for solid-liquid: 0.18 J/m²

c for liquid-gas: 0.34 J/m²
stens= 2.14d3

c monomer volume, diameter and area
xvo=xmwp/(xrhop*xav)
xdo=(6.0d0*xvo/xpi)**(1.0d0/3.0d0)
xao=6.0d0*xvo/xdo
c TTIP mass consumption (g/h)
xmassttip=21.d0
c Volumetric flowrates (l/min, standard)
xqAr=0.65d0
xqN2=4.3d0
xqCH4=0.4d0
xqO2 = 1.2d0

c Molecular weights (g/mol)
  xmwAr = 40.0d0
  xmwN2 = 28.0d0
  xmwCH4 = 12.0d0
  xmwO2 = 32.0d0
  xmwTTIP = 283.88d0

c Universal gas constant (l*atm/mol/k)
  univr = 0.082d0

c Reference temperature (K) and Pressure (atm)
  tstand = 298.0d0
  pstand = 1.0d0

c Total gas mass flowrate (g/min)
  xmgases = (pstand/univr/tstand) * (xqAr*xmwAr + xqN2*xmwN2 + xqCH4*xmwCH4 + xqO2*xmwO2)

c For the TTIP case c0 is in molecules/gr-gas
  xno = xmassttip/60.0d0/xmwTTIP/xmgases \times a

c TiO2 number concentration (#/g-gas)
  y(1) = 1.0d-15

c TiO2 area concentration (cm2/g-gas)
  y(2) = xao*1.0d-15

c TiO2 volume concentration (cm3/g-gas)
  y(3) = xvo*1.0d-15

c TTIP concentration (molecules/g-gas)
  y(4) = xno

c particle temperature (K)
  y(5) = 400.0d0

c Total distance from burner face (cm)
  rtm = 20.0d0

c Solver Parameters
  h = 1.0d-20
  lrw = 10000
  liw = 10000
  ieq = 5
  itol = 1
  rtol = 1.0d-4
  atol = 1.0d-150
  t = 0.0d0
  imeth = 21

c iwk(1) = 1

c iwk(2) = 1

c iwk(3) = 0

c iwk(4) = 0

c itask = 4

c istate = 1

c
open(unit=21, file='hen21ssikzks-a.txt')
open(unit=22, file='hen21ssikzks-b.txt')

c
10 if (t.lt.1.0d-4) then
   tend = t + 1.0d-5
else if (t.lt.1.0d-3.and.t.ge.1.0d-4) then
   tend = t + 1.0d-4
else if (t lt 1.0d-2.and.t ge 1.0d-3) then
   tend = t + 1.0d-3
else if (t lt 1.0d-1.and.t.ge.1.0d-2) then
   tend = t + 1.0d-2
elseif (t.lt.1.d0.and.t.ge.1.d-1) then
tend = t + 1.d-2
elseif (t.lt.rtm.and.t.ge.1.d0) then
tend = t + 1.d-1
endif

c additional solver parameters
rwk(1)=tend
iopt=1
rwk(5)=h
c iwk(6)=100000
c iwk(7)=0

call vodpk(fcn,ieq,y,t,tend,itol,rtol,atol,istask,istate,iopt,
2 rwk,lrw,iwk,liw,jac,psol,imeth,1.0,1)

c volume equivalent diameter of aggregate (nm)
xdav=((6.d0/xpi*y(3)/y(1))**(1.d0/3.d0))*1.d7

c area equivalent diameter of aggregate (nm)
xdas=(dsqrt(y(2)/y(1)/xpi))*1.d7

c primary particle diameter (cm)
xpdp=6.d0*y(3)/y(2)

c number of primary particles xnp
xnpp=(y(3)/y(1))/(xpi*(xpdp**3.d0)/6.d0)

write(6,100) tend,t,tem,y(4),y(5)
call flush(6)
write(21,100)tend,xdav,xpdp*1.d7,xnpp,y(4),y(1),y(2)
call flush(21)
write(22,100)tend,t,tem,y(5)
call flush(22)

if (t.lt.rtm) go to 10
100  format(1x,7(e12.6,1x))
99   stop
end

Subroutine FCN

subroutine fcn(ieq,t,y,yp,rpar,ipar)
implicit doubleprecision(a-h,o-z)
dimension y(5),yp(5),rpar(*),ipar(*)

common/block1/xno,xpd,xrc,r,p
common/block2/xav,xkb,xpi,vel
common/block3/xmwp,xrhop,xsigma,xekb,xmwg
common/block4/xdf,xnp,xpdm,xcol,xrhog,xsin
common/block5/x1,x2,x3,x4,x5,x6
common/block6/xvo,xdo,xao,tem
common/block7/xrrt,xrrs,xrg
common/block8/ctio2,sbolt,emis,stens

Temperature (K)
if(t.lt.0.25d0) then
tem=8294.3852d0*t+400.d0
else
  ua=2509.5051d0
  ub=-704.4758d0
  uc=88.0521d0
  ud=-2.6516d0
  ue=-0.2337d0

uf=0.0264d0
ug=-0.0002d0
tem=(ua+ub*t+uc*t**2.d0+ud*t**3.d0)
* /(1.d0+ue*t+uf*t**2.d0+ug*t**3.d0)
endif

c Reference temperature (K)
tref=298.15d0
c Total inlet flow-rate (cm^3/s)
xqtot=6.55d0*1000.d0/60.d0
c Burner diameter (cm)
xdtube=2.5d0
c Velocity (cm/s) (Pressure=const=1 atm)
vel=4.d0*xqtot/(xpi*xdtube**2.d0)*tem/tref
c gas density, rhog gr/cm^3
xrhog=(p*xmwg/r/tem)/1000.d0
(c Chapman-Enskog)
tstar=tem/xekb
c omega
omega=(x1*tstar**(-x2))+x3*dexp(-x4*tstar)
* +x5*dexp(-x6*tstar)
c viscosity xmu in gr/sec/cm
xmu=(2.6693d-25)*dsqrt(xmwg*tem)
* /(xsigma*xsigma*omega)
c kinematic viscosity, xnu (cm^2/s)
xnu=xmu/xrhog
c gas mean free pathm xlam (cm)
xlam=xnu*dsqrt(xpi*xmwg/
* (2.0d0*8.31441d7*tem))
c This is the ideal gas law universal constant in cgs
rgas = 8.31451d7
c Specific heat cp of air (Turns, 1996; pp 541) in cm^2*g/s2/K/
IF (tem.GT.300.d0.AND.tem.LT.1000.d0) THEN
cpN2=(0.03298677d2+tem*0.14082404d-2
* +(tem**2.d0)*(-0.03963222d-4)+(tem**3.d0)*0.05641515d-7
* +(tem**4.d0)*(-0.0244485d-10))*rgas/xav
cpO2=(0.03212936d2+tem*0.11274864d-2
* +(tem**2.d0)*(-0.05756150d-5)+(tem**3.d0)*0.13138773d-8
* +(tem**4.d0)*(-0.08768554d-11))*rgas/xav
ELSEIF (tem.GE.1000.d0.AND.tem.LT.5000.d0) THEN
cpN2=(0.02926640d2+tem*0.14879768d-2
* +(tem**2.d0)*(-0.05684760d-4)+(tem**3.d0)*0.10097038d-9
* +(tem**4.d0)*(-0.06753351d-13))*rgas/xav
cpO2=(0.03697578d2+tem*0.06135167d-2
* +(tem**2.d0)*(-0.12588420d-6)+(tem**3.d0)*0.01775281d-9
* +(tem**4.d0)*(-0.11364354d-14))*rgas/xav
END IF
Thus, for cp-air (Reid et al., 1987; pp 121) in cm²*g/s²/k#
cpair=0.21d0*cpO2+0.79d0*cpN2

c primary particle diameter xpd (cm)
  xpd=6.0d0*y(3)/y(2)

c primary particle volume xvp (cm³)
  xvp=xpi*(xpd**3.d0)/6.d0

c number of primary particles xnp
  xnp=(y(3)/y(1))/xvp

c collision radius, xrc (cm)
  xrc=xpd/2.0d0*(xnp**(1.0d0/xdf))

c Knudsen number, xkn
  xkn=xlam/xrc

c diffusion coefficient, xdif (cm²/s)
  xdif=xkb*tem/6.0d0/xpi/xmu/xrc*
      *(5.0d0+4.0d0*xkn+*
       6.0d0*(xkn**2.0d0)+*
       18.0d0*xkn**3.0d0)/
      *(5.0d0-xkn+(8.0d0+xpi)*
       **2.0d0))

c particle velocity, xpc (cm/s)
  xpc=dsqrt(8.0d0*xkb*tem/xpi
    /xrhop/(y(3)/y(1))))

c particle mean free path, xl (cm)
  xl=8.0d0*xdif/xpi/xpc

c transition parameter, xg
  xg=1.0d0/6.0d0/xrc/xl*
      *(2.0d0*xrc+xl)**3.0d0
      *(4.0d0*xrc*xrc+xl*xl)**(3.0d0/2.0d0)
      *-2.0d0*xrc

c collision kernel, xcol (cm³/s)
  xcol=8.0d0*xpi*xdif*xrc/
      *(xrc/(2.0d0*xrc+(dsqrt(2.0d0))))*xg
      +(dsqrt(2.0d0))*xdif/xpc/xrc)

c sintering time (s) estimation

c xpd (primary particle diameter) in cm

From Kobata et al. (1991) as cited by Xiong et al (1993)
xsin=(7.4d8)*y(5)*(xpd**4.d0)*dexp(31000.d0/y(5))

For the overall rxn, xrrt (s⁻¹)
(thermal decomposition, Okuyama et al., 1990)
xrrt=(3.96d5)*dexp(-70.5d3/8.314d0/tem)

For surface rxn, xrrs (cm/s)
(Battiston et al., 1997)
xrrs=(1.d11)*dexp(-126.d3/8.314d0/y(5))

if (xrrs*y(2)*xrhog/xrrt.ge.1.d0) then
  xrg=0.0d0
c New surface rxn
xrrs=xrrt/(y(2)*xrhog)
else
c For the gas phase rxn, xrg (s-1)
xrg=xrrt
 -xrrs*y(2)*xrhog
endif
c System of differential equations

yp(1)=-0.5d0*xcol*y(1)*y(1)*xrhog/vel
 * +xrg*y(4)/vel
xparam=1.d0
yp(2)= -xparam*(1.d0/xsin)*
 * (y(2)-(((y(3)/y(1))/xvo)**(2.d0/3.d0))*xao*y(1))/vel
 * +xrg*y(4)*xao/vel
 * +xrrs*y(4)*4.d0*xpi*y(1)*xnp*xpd*xvo*xrhog/vel
yp(3)=0.0d0
 * +xrrt*y(4)*xvo/vel
yp(4)=-xrrt*y(4)/vel

c This is the pressure of 1 atm in cgs
pcgs = 1.01325d6
c Lehtinen and Zachariah (2002)
yp(5)=0.d0
 * +(stens/xsin*((xpi*xpd**2.d0)*xnp
 * -xpi*((6.d0/xpi*y(3)/y(1))**(2.d0/3.d0)))*cpair
 * -pcgs/dsqrt(2.d0*xpi*xmwg/xav*xkb*tem)*cpair
 * +emis*sbolt*xpi*((6.d0/xpi*y(3)/y(1))**(2.d0/3.d0))*(y(5)-tem)
 * )/(Stio2/(y(3)/y(1))/xvo)/vel
return
don

c SOLVER
SUBROUTINE VODPK (F,NEQ,Y,T,TOUT,ITOL,RTOL,ATOL,ITASK,
1 ISTATE,IOPT,RWORK,LRW,IWORK,LIW,JAC,PSOL,MF,RPAR,IPAR)
EXTERNAL F,JAC,PSOL
DOUBLE PRECISION Y,T,TOUT,RTOL,ATOL,RTOL,ITASK,ISTATE,IOPT,RWORK,LRW,IWORK,LIW,JAC,PSOL,MF,RPAR
INTEGER NEQ,ITOL,ITASK,ISTATE,IOPT,LRW,IWORK,LIW,IPAR
DIMENSION Y(*),RTOL(*),ATOL(*),RWORK(LRW),IWORK(LIW),
1 RPAR(*),IPAR(*)

APPENDIX K
K.1. Monodisperse code for silicon coalescence heat release

c CGS UNITS

c Si Nanoparticles

program si6

implicit doubleprecision (a-h, o-z)
dimension y(5), iwk(10000), rwk(10000)
external fcn

common/block1/xav, xkb, xpi
common/block2/xmwp, xmwg, tem
common/block3/csi, sbolt, emis, stens
common/block4/xn, xasph, xsin, xsino
common/block5/cpar

Gas properties refer to Ar
Reference conditions: standard: 298.15 K, 1 atm

data xav, xkb, xpi /6.022137d23, 1.38066d-16, 3.1415926d0/
data xmwp, xmwg /28.d0, 40.d0/

Constant gas temperature (K)
tem = 600.d0

Number of monomers (atoms) per particle
xn = 100.d0

Primary particle diameter (cm)
xdm = 1.6d-7

Area of spherical aggregate (cm2)
xasph = xpi * xdm * xdm * (2.d0** (2.d0 / 3.d0))

Unitless area
y(1) = (2.d0 * xpi * xdm** 2.d0 - xasph) / xasph

Unitless temperature
y(2) = 0.0d0

Total unitless time
rtm = 3.d0

Solver Parameters
h = 1.0d-90
lrw = 10000
liw = 10000
ieq = 5
itol = 1
rtol = 1.d-6
atol = 1.d-200
t = 0.d0
imeth = 21

iwk(1) = 1
iwk(2) = 1
iwk(3) = 0
iwk(4) = 0
itask = 4
istate = 1
open(unit=21,file='si6-a.txt')

10 if (t.lt.0.5d0) then
    tend = t + 1.d-3
elseif (t.lt.1.d0.and.t.ge.0.5d0) then
    tend = t + 1.d-2
elseif (t.lt.rtm.and.t.ge.1.d0) then
    tend = t + 1.d-1
endif

c additional solver parameters
rwk(1)=tend
iopt=1
rwk(5)=h
iwk(6)=10000
c iw(7)=0

call vodpk(fcn,ieq,y,t,tend,itol,rtol,atol,itask,istate,iopt,
      rwk,lrw,iwk,liw,jac,psol,imeth,1.0,1)

write(6,100) tend,y(1),y(2)*tem+tem
call flush(6)
write(21,100)tend,y(1),y(2)*tem+tem,stens
call flush(21)

if (t.lt.rtm) go to 10
100 format(1x,7(e12.6,1x))
99 stop
end

c Subroutine FCN
subroutine fcn(ieq,t,y,yp,rpar,ipar)
c implicit doubleprecision(a-h,o-z)
dimension y(5),yp(5),rpar(*),ipar(*)

commn/block1/xav,xkb,xpi
commn/block2/xmwp,xmwg,tem
commn/block3/csi,sbolt,emis,stens
commn/block4/xn,xasph,xsin,xsino
commn/block5/cpar

c Melting point of Si (K)
tmelt=1500.d0
c Particle temperature (K)
tpart=y(2)*tem+tem
c Si Specific Heat (assuming: cv=cp)
in cm2*g/sec2/K/
if (tpart.lt.tmelt) then
    csi=0.89d0*xmwp*1.d7/xav
else
    csi=1.2174d0*xmwp*1.d7/xav
endif
c Stefan Boltzmann constant (Holman, 1997; last page), in g/K4/s3
sbolt=5.669d-5
c Si emissivity (Approximation from Holman, 1997; pp 651-652)
emis=0.0d0
c Si surface energy in g/s2
stenso=0.985d3
stens=stenso*(1.d0+0.068d0*(1.d0-tpart/4000.d0)*
   *dexp((tpart-tmelt)/tmelt))

c  This is the ideal gas law universal constant in cgs
rgas = 8.31451d7

c  Specific heat of Ar in cm2*g/s2/k/
par=20.8d0*1.d7/xav

c  Diffusion coefficient at Tp (cm2/s)
xdiff=(4.69d-3)*dexp(-7562.d0/(y(2)*tem+tem))

c  Diffusion coefficient at Tg (cm2/s)
xdiffo=(4.69d-3)*dexp(-7562.d0/tem)

c  tau (s)
xis=3.d0*xkb*tem*xn/64.d0/xpi/stens/xdiff

c  tauo (s)
xiso=3.d0*xkb*tem*xn/64.d0/xpi/stens/xdiffo

c  This is the pressure of 1 atm in g/s2/cm
pcgs = 1.01325d6

c  Gas-particle collision rate (in CGS) (#/s)
xz=pcgs*xasph/dsqrt(2.d0*xpi*xmwg/xav*xkb*tem)

c  Other group parameters
xes=stens*xasph
xeb=2.d0*csi*xn*tem
xeg=xiso*xz*par*tem

c  Differential Equations

yp(1)=-(xiso/xis)*y(1)

yp(2)=(xes/2)*xiso/xis*y(1)-(xeg/2)*y(2)

return
end

SOLVER

SUBROUTINE VODPK (F,NEQ,Y,T,TOUT,ITOL,RTOL,ATOL,ITASK,
1  ISTATE,IOPT,RWORK,LRW,IWORK,LIW,JAC,PSOL,MF,IPAR)
EXTERNAL F,JAC,PSOL
DOUBLE PRECISION Y,T,TOUT,RTOL,ATOL,RWORK,RPAR
INTEGER NEQ,ITOL,ITASK,ISTATE,IOPT,LRW,IWORK,LIW,MF,IPAR
DIMENSION Y(*),RTOL(*),ATOL(*),RWORK(LRW),IWORK(LIW),
1   RPAR(*)}
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