

RESIDENCE-TIME-FIXED INVESTIGATION OF PRESSURE AND
TEMPERATURE EFFECTS ON THE FLAME SYNTHESIS OF NANOPARTICLES

By

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ABSTRACT OF THE THESIS

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The synthesis of nano-titania ($n\text{-TiO}_2$) is investigated experimentally and computationally in low-pressure $\text{H}_2/\text{O}_2/\text{inert(s)}$ burner-stabilized flat flames with strategic helium/argon/nitrogen dilution in a stagnation point geometry, using a metal-organic (titanium tetra-isopropoxide, TTIP) precursor. Gas-phase simulation is applied to compute various experimental flame structures. The employment of combinations of different molecular weight and specific heat capacity inert gases makes it possible to tailor the flame structure, so as to isolate various known parameters affecting particle growth, while maintaining fixed gas-phase residence time. Using this method, the effects of ambient pressure and temperature are studied. Two particle growth and evolution sub-models (i.e. a monodisperse model and a sectional model), which utilize the gas-phase modeling results, calculate the primary and aggregate particle sizes as a function of axial location in the flow field. After deposition on a cooled substrate, the powders are characterized *ex-situ* using X-ray diffraction (XRD) and Brunaur-Emmet-Teller (BET) measurements to determine nanopowder characteristics, such as phase/crystallinity and specific surface area (from which primary particle size can be inferred). This study indicates that pressure, with other parameters fixed, has limited effect on particle growth.

With identical temperature histories at 20, 30, and 40torr, the primary particle sizes vary by less than 1nm, computationally, and less than 0.8nm experimentally. In contrast, temperature, with other parameters fixed, plays a significant role in primary particle development. Particles generated in strategically diluted flames, with only an 80K difference in maximum temperature, have primary sizes that are more than 2.5nm different.

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Chapter 1

Introduction

Nanostructured materials are a promising technology of the future for which many possible applications have been suggested. Interest in commercial applications of these novel nanomaterials has fueled the realm of science and engineering to develop them. It should be noted that the applications of these advanced materials are highly dependent upon their chemical composition, size range, and morphology. The need to control these parameters requires customized synthesis processes that are capable of producing these nanomaterials at high-rates and with high efficiency.¹

Included in this new class of materials are nanopowders with particle sizes in the 1 to 50nm range.^{1,2} In this size range, there are three major areas where the grain size directly affects the properties of these novel materials. These three areas include: the overlap of the grain size with the characteristic physical length, the increased role of interfacial defects due to the nanometer scale crystalline size, and the fact that other properties play a role in characterizing the grain boundaries of these materials.² Not only the size but also the shapes of these particles strongly influence the vast majority of their properties including optical, electrical, and magnetic properties. In addition, there are noticeable effects in characteristics such as the hardness, toughness, and melting points of these nanomaterials as compared to their bulk material counterparts.¹ Extreme variations in material properties can be exploited in applications including uses as heterogeneous

catalysts, photocatalysts, gas sensors, pigments in paints and cosmetics, corrosion-protective coatings, optical coatings, ceramics, electric devices such as varistors, and solar cells for the production of hydrogen and electric energy.³

Many nanomaterials are of interest, but the main material studied here is titanium dioxide (TiO_2). This particular material has been emphasized in part due to the fact that it is non-toxic and safe for the lab environment and its handlers. Titania has three different crystallinities: rutile, anatase, and brookite. Rutile titania is the most widely used form of titania and enjoys widespread use in virtually every kind of paint due to its high refractive index. Anatase titania is actively pursued in applications for photo-assisted degradation of organic molecules. This results in its use in a plethora of areas including water purification, wastewater treatment, disinfection in hospitals, self-cleaning coatings on car windshields, protective coatings on marble, and is even applied to the slowdown or halting of the growth of tumor cells as studied in rats.³ Gas-sensing of oxygen by way of semi-conducting TiO_2 has been studied as it pertains to its use in regulating the air/fuel mixture in car engines. Thin film coatings of titania have been applied as antireflective coatings, dielectric mirrors for lasers, metal mirrors with enhanced reflection, and filters. Finally, TiO_2 is being studied extensively as its high dielectric constant could make it an ideal candidate as an ultrathin metal oxide to replace SiO_2 as the best dielectric gate available.³

1.1 Motivation and objectives

There are a myriad of techniques available for the production of nanostructured materials. Methods involving flame processes are typically used to manufacture these nanomaterials

in commercial quantities since the process includes a high level of scalability.⁴ While this method shows great promise, there are a number of drawbacks that can limit its success. First and foremost is the utilization of a complex combustion process. Particle characteristics are strongly dependent on numerous combustion process variables and determined all within a few milliseconds.⁴ Many in the research and development communities have thoroughly studied the complex process of flame synthesis of nanomaterials, but there are still many questions without answers. The objective of this body of work is to explore more closely the relationship between pressure and temperature and final particle characteristics. A strategic experimental configuration with accompanying flame structure simulation gives insight into the actual material processing flow field. Recent work involving non-intrusive laser-based diagnostics has verified the accuracy of these flow field simulations. In this particular case, a premixed flat flame in a stagnation point geometry has been used to synthesize TiO_2 powders in low pressure environments.

Simply understanding the flow field in which the particles are produced will not be sufficient enough to aid in scale-up of these processes. Given the conditions of the flow field, simulations have been employed that model the growth of the particles as they travel through the flame. These models allow researchers to better predict the outcome for any given set of flame conditions and can give valuable insight into the fundamentals that control particle inception and growth. Accurate predictions resulting from the aforementioned particle growth simulations can aid in scale-up from laboratory process to commercial production of these novel nanomaterials.

Conversion of vapor precursor to ultrafine particles involves a variety of physical and chemical phenomena. As a result, the employed growth models must accurately describe the physical and chemical aspects of particle inception, ensuing transport of the particles through the flow field as they develop, and interactions between the particles themselves as well as between the particles and their surrounding gaseous combustion environment. This work employs flow field descriptions that, in turn, are used to address particle nucleation and transport during its residence in the flame as well as development of the particles as affected by coagulation, coalescence, and surface growth.

1.2 Strategies and innovations in this work

In this study, metal-organic liquid precursor (titanium tetra-isopropoxide), carried by a gas, is pyrolyzed and converted into ceramic nano-TiO₂ particles in the flame in a low pressure environment. One primary concern in the production of these nanophase materials is the undesirable formation of particle agglomerates. Masses of nanoparticles lose their benefits as the products stray away from having nano-scale crystallinity and narrow size distribution. Methods are still being perfected that promise high-yield, high-quality, non-agglomerated powders that exhibit narrow particle size distributions.

Flames in low-pressure environments offer a number of advantages over their atmospheric pressure counterparts. It has been noted that the precursor decomposition temperatures are lower and particle residence times are diminished. Both of these factors contribute to a significant reduction in particle to particle collisions. The reduced number of collisions between particles hampers the undesirable process of agglomeration.⁵

The inherent uniformity of the flat flame configuration coupled with the presence of thermophoretic forces resulting from large temperature gradients near the substrate are a major advantage associated with this particular synthesis configuration.⁶

1.3 Overview

Experimental and computational methods have been applied in this body of work to study the synthesis of nano-titania ($n\text{-TiO}_2$) in a low pressure environment utilizing a $\text{H}_2/\text{O}_2/\text{N}_2$ burner-stabilized flat flame in a stagnation point geometry resulting from the presence of a cooled substrate. The metal-organic precursor used throughout these experiments is titanium tetra-isopropoxide (TTIP). Other inert gases (e.g. helium and argon) are used to alter flame characteristics so as to determine the effects of pressure and temperature on the nanoparticles produced. This particular flame configuration is used in order to take advantage of its quasi one-dimensional, stagnation-point geometry which facilitates data collection, analysis, and interpretation. The main objective behind this work is to provide further insight into the process of tailoring nanoparticles through control of process parameters. In order to do this, steps are taken to define accurately the flow field characteristics, to model the particle growth through computational simulation, and to characterize the as-produced nanoparticles resulting from the given conditions. The phase and crystallinity are determined by use of X-ray diffraction (XRD) and primary particle size is determined by application of the Braunauer-Emmet-Teller (BET) method. A flow field simulation and two particle growth models are used to simulate all of the experimental cases detailed in this work.

A modified Sandia SPIN code is used to determine the flow field description. The model incorporates a detailed chemical kinetics mechanism and transport module in order to compute species, temperature, and velocity profiles in the flow field. The accuracy of the SPIN code results as compared to the actual experimental setup has been previously verified using laser-induced fluorescence (LIF) to map gas-phase temperature and OH radical concentrations. The complete description of the flow field is determined through the use of equations for radial and circumferential momentum, thermal energy, and chemical species in conjunction with the continuity equation and a pressure-explicit equation of state. Three modules are used concurrently in the SPIN code: CHEMKIN for gas-phase kinetics, SURFACE CHEMKIN for surface chemical kinetics, and TRANSPORT for variable transport properties. A chemical kinetics mechanism for hydrogen flames involving 9 species and 21 elementary gas-phase reactions is employed. The following boundary conditions are applied:

- (1) experimentally specified inlet mass flux and temperature at the burner;
- (2) no-slip condition and constant surface temperature at the substrate;
- (3) recombination of H, O, OH, and HO₂ with unit sticking probability at the substrate surface; and
- (4) gas-phase mass flux, including diffusive and convective processes of each species to the substrate, balanced by the creation or depletion of that species by surface reactions.

Two particle growth models are applied in this work to compare with each other and with experimental results. The first is a monodisperse model. This model is simpler than a more robust sectional model, as it neglects the polydispersity of the primary and aggregate particles. This means that particle growth is only a result of coagulation and coalescence. The monodisperse model makes the following assumptions:

- (1) the precursor decays instantaneously at a fixed temperature of 800K;
- (2) homogeneous nucleation of particles occurs at the critical size of 0.4nm;
- (3) particle velocity is the same as the corresponding gas-phase velocity at the location of instantaneous homogeneous nucleation;
- (4) only a negligible difference exists in time and temperature histories of particles nucleating at different distances from the centerline.

A more robust sectional model takes into consideration factors including precursor decomposition, nucleation, and particle to particle collisions resulting in coagulation, coalescence, and surface growth. The model evaluates the primary particle size, aggregate particle size, and geometric standard deviation. A 102 size section model with a geometric spacing factor q of 1.2 on a logarithmic volume scale is applied. Average primary particle size is calculated after the application of an equation of average surface area is added to the volume sectional model.

Starting with previous studies of the pressure effect on the particle growth, care is taken to further isolate pressure as the only varying parameter during synthesis. Previously,

inlet velocities of cold gases at the burner differed under different pressure conditions. Consequently, gas-phase velocity profiles were not identical, which in turn caused the particle residence times in the hot flame zones to be different. In this study, the inlet velocities are specified to be the same, where inert helium gas (given its low heat capacity and molecular weight and high diffusivity) is added such that the flame structure remains essentially the same, matching the temperature profiles and velocity profiles for the three different pressure conditions.

The next step is to fix the pressure and to probe only the temperature effect on the growth of the nanoparticles. In a similar fashion as with the pressure study, inert gases are again introduced to manipulate the flame structure. This time, the inert gases are added in an effort to match the velocity profiles but purposefully leave a difference in the temperature histories. Specifically, helium and argon are both added to the already-present N_2 diluent in order to obtain a decrease in temperature at every point between the burner and the substrate. In the second case, helium and argon are added and the original N_2 diluent is removed completely in order to obtain a similar temperature profile with only the use of inert diluents. In addition to the experimental cases, a purely computational approach is taken to assess the temperature effect by directly swapping the temperature profile used in the particle growth model. This aided in determining whether the temperature differences or the presence of the inerts is playing the most significant role in the particle growth.

1.4 Outline of this thesis

Chapter 2 gives a brief background of other work that has been done involving flame synthesis of nanomaterials and the effects on particle size due to controlled process parameters. Detailed descriptions of the key elements of the experimental setup, standard operating procedures, and characterization are given in Chapter 3. A comprehensive flame structure model, including detailed chemical kinetics and transport modules, is applied which is then coupled with two different models for particle growth. The monodisperse and sectional models describe the evolution of the particle from precursor decomposition, to homogeneous nucleation, to the development of the particle through coagulation, coalescence, and surface growth. Three standard cases have been defined in order to establish preliminary trends and to provide a baseline for the pressure and temperature studies to follow. These three standard cases are described in Chapter 5. Chapter 6 explores the pressure effect on the synthesis of the nanoparticles, and Chapter 7 examines the temperature effect on the synthesis of the nanoparticles. Concluding remarks and suggestions for future work are given in Chapter 8.

Chapter 2

Literature Review

In recent years, many techniques for the manufacture and synthesis of an extensive variety of nanoparticles have been studied. Methods involving gas-phase synthesis are perhaps the most common due to a variety of advantages. The purity of gas-phase processes is maintained by avoiding the use of liquids with trace minerals. The fast chemical reaction rates are relied on to preserve the purity of the product. However, complete understanding of the fundamental growth mechanisms driving the synthesis of these nanomaterials has still escaped the scientific community. Understanding the controlling parameters and their effects on particle size and crystallinity will help turn the production of simple powders into the fabrication of functional materials that have applications outside of the laboratory.

Natural inhibitors to the various gas-phase techniques including small time scales, high temperatures, temperature gradients, and aggressive gaseous environments make experimental measurements of the controlling parameters extremely difficult. For this reason, several computational models have been developed and employed to simulate particle growth and evolution in an effort to improve general understanding of the growth mechanisms and also to aid in optimizing the synthesis process for high-yield and high-purity products.

This literature survey introduces the fundamentals of gas-phase synthesis and looks into parameters that are investigated and their effects on particle sizes and morphologies.

2.1 An introduction to gas phase synthesis

Gas-phase synthesis techniques rely on the thermodynamically unstable condition of a vapor precursor that will readily form solid material. The nucleation of solid particles directly from the gas-phase is a major factor in maintaining product purity. Synthesis conditions are purposely chosen to create a high level of supersaturation where the solid phase is thermodynamically favorable as compared to the gas-phase precursor. Without the aid of any foreign surfaces, this process results in homogeneous nucleation. Once solid particles have been formed, the still-supersaturated conditions will be relieved by nucleating additional monomers onto the surfaces of the existing monomers which will generate clusters. Generally, monomer clusters larger than a critical size are considered nanoparticles.

There are four major growth mechanisms: (1) particle inception, (2) surface growth, (3) coagulation, and (4) coalescence. Particle inception is the process described above, where physical condensation of vapor precursors generates solid monomers. Surface growth can be either the addition of mass via condensation onto the surface of an already-existing monomer or cluster or it can be the loss of mass via vaporization of a monomer back into the gas-phase. Coagulation refers to the collision of two or more particles generating points of contact shared on their surfaces. This growth mechanism is driven by the Brownian motion of the particles. Coalescence, or sintering, is the fusion of

collided particles which are sharing points of contact on their surface. This mechanism is the logical follow-up to coagulation and occurs at high temperatures.

2.2 Controllable synthesis parameters and their observed effects

One of the many benefits to gas-phase synthesis techniques is their high level of controllability. Several parameters and their effects on particle characteristics have been investigated in the literature. Among these parameters are pressure, temperature, residence time, precursor-loading rate, and electric field application. Most of the information currently available regarding the synthesis of nanoparticles in combustion synthesis environments is due to thorough and systematic investigations of these system parameters. With a clearer understanding of the fundamentals of the growth mechanisms behind the synthesis of nanoparticles, researchers are moving on to more advanced methods of controlling particle morphology and composition such as electric fields and mixed-oxide systems.⁷

Some of the most important controllable parameters are particle precursor concentration and the combination of the temperature history and residence time of the particles in the combustion environment. Secondary parameters, including flame stoichiometry, diluent concentration, and gas flow rates, can be optimized insofar as they affect the major parameters of temperature history and particle residence time.⁷ Increases in primary particle sizes and decreases in specific surface area have been observed with increasing precursor-loading rates. These effects are decidedly a result of increased agglomeration of larger primary particles.^{8,9,10} Zachariah *et al.*⁸ reported surface growth as the enhanced growth mechanism over particle homogeneous nucleation. Larger primary particles form

aggregates with lower surface areas.⁷ Pratsinis *et al.*¹⁰ concluded that the increase in precursor-loading concentration generates an increase of individual agglomerates. This creates more points of contact between primary particles and allows for a more rapid sintering process leading to increased primary particle sizes and a decrease in specific surface area.⁷

Temperature effects are decidedly more unpredictable insofar as researchers have uncovered. Temperature appears to be coupled strongly with residence time. Pratsinis *et al.*¹⁰ observed that increasing fuel flow rates raises the flame temperature and causes a longer residence time for the particles in the flame. This combination effects an increase in rutile weight fraction of the sample.¹⁰ More readily observable is the increase in thermal decomposition of vapor precursor at high temperatures. This generates a higher concentration of monomers which can then readily sinter to form aggregates under high temperatures. Coupled with longer residence times, these agglomerates would have time to coalesce fully into larger primary particles.⁷

Low-pressure environments for combustion synthesis of nanoparticles are widely considered to be advantageous. These strategic environments allow for low levels of particle agglomeration due to reduced frequency of inter-particle collisions and suggest an ability to easily scale-up the process. The keys to gas-phase methods of nanoparticle synthesis are low pressure environments and controllable time/temperature histories experienced by the synthesized particles.¹¹ Flat flames operating at low pressures in stagnation point geometries can generate a vast selection of temperature histories and

particle residence times. Flame parameters such as fuel and oxidizer, stoichiometric ratio, flow rate, diluents, substrate-burner gap distance, and cooled substrate temperature can all be used to fix time/temperature histories for synthesized particles.¹²

Chapter 3

Experimental Setup

The experimental part of this work revolves around the use of a premixed flat flame in a low-pressure environment. The flame is burner-stabilized where the combustion gases $\text{H}_2/\text{O}_2/\text{N}_2$ enter the chamber with, in some cases, a combination of inert gases (i.e. helium and/or argon). A flat flame is utilized in order to facilitate ease of computational modeling. It can be reasonably assumed that particles nucleating at different radii from the centerline experience similar trajectories and also time/temperature histories. The products of combustion proceed downward and finally impinge on a water-cooled substrate plate. This substrate plate is responsible for the creation of a stagnation-point flow-field in the flame. Metal-organic liquid precursor is bubbled and carried into the flame by entrainment in a hydrogen carrier gas. Once in the flame, the precursor vapor decomposes into radicals that are oxidized and then condensed into solid-phase nano- TiO_2 particles. The particles are then aided by the thermophoretic effect in depositing on the cooled substrate plate. The relatively low temperatures in the flame assist in the condensation of nano-sized particles due to the supersaturated conditions in the flame. The low-pressure environment is conducive to reducing particle residence time in the hot zone of the flame as well as reducing inter-particle collisions. This in turn allows for smaller primary and aggregate particle sizes to be obtained.

This chapter details descriptions of the different aspects of the experimental setup as well as a standard operating parameters and procedures. In addition, descriptions of the ex-situ powder characterization techniques are given.

3.1 Flame synthesis configuration

The main components of the flame synthesis experiment are the burner, precursor delivery unit, water-cooled substrate, pressure control technique, and the low-pressure synthesis chamber. A schematic of the setup is shown in [Figure 3.1](#), and photographs of the actual setup can be seen in [Figure 3.2](#) and [Figure 3.3](#).

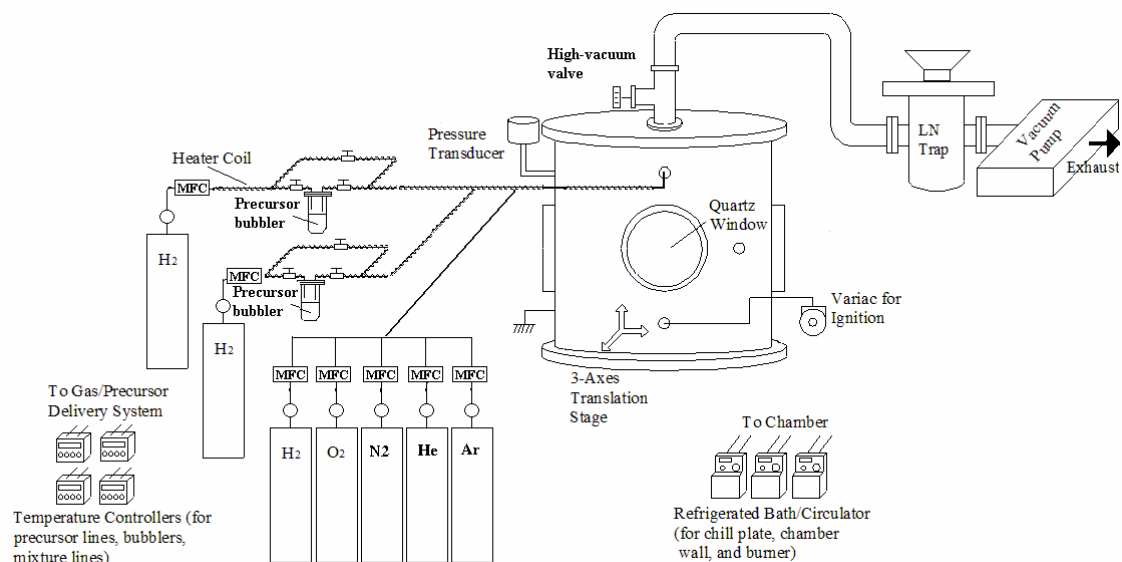


Figure 3.1. Schematic of the experimental setup with a precursor bubbler for TTIP and future work with silver doping.

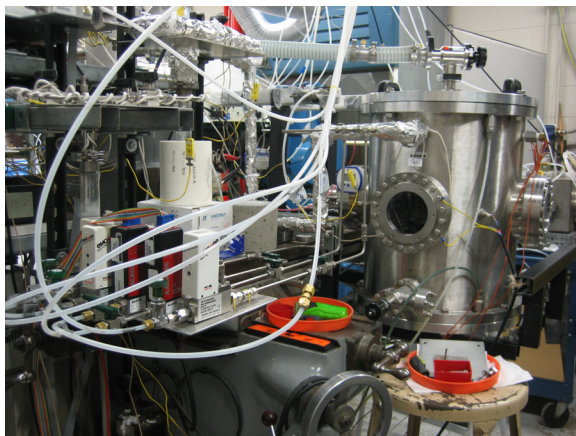


Figure 3.2. Photograph of the actual experimental setup found in the laboratory.

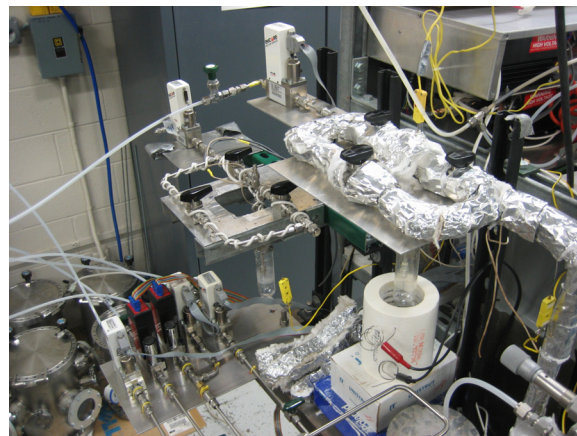


Figure 3.3. Photograph of the mass flow controllers and TTIP precursor delivery line. An additional precursor line for silver doping is present, but not yet functional.

3.1.1 Flat flame burner

The burner is constructed from a thick aluminum plate with water channels machined out to facilitate cooling. The burner is mounted by supporting arms on two long vertical screws which are attached to a disk at the bottom of the chamber that is free to move about the bottom of the chamber. The face of the burner points downward and contains a hexagonal pattern of 360 holes which are 1mm in diameter. On top of the burner plate is small mixing chamber where the $\text{H}_2/\text{O}_2/\text{N}_2$ and inert gases are premixed.

The water bath used for cooling the burner is well-maintained at 80°C for each run. The temperature can be monitored during the experiment by a K-type thermocouple and temperatures have been observed around 120°C . The purpose of cooling the burner is to prevent precursor condensation and clogging of the burner holes. Nonetheless, the holes are cleaned after each run using a thin wire. The water-cooled substrate is located directly below the burner.

3.1.2 Flame establishment

The gases enter a mixing chamber attached to the top of the burner plate. After mixing, the combustible gases, diluent, and inert gases exit the burner and establish a burner-stabilized, axisymmetric, stagnation-point premixed flame. A depiction can be seen below in [Figure 3.4](#). A feedthrough rotator is located outside of the chamber and is connected to an arm inside the chamber that swings an igniter into the flame zone. The igniter consists of a nichrome wire wound around a small ceramic rod for stability and form. A variac applies 25% of 120VAC across the nichrome wire. Once the flame is ignited, the igniter is retracted out of the flow field and off to the side.

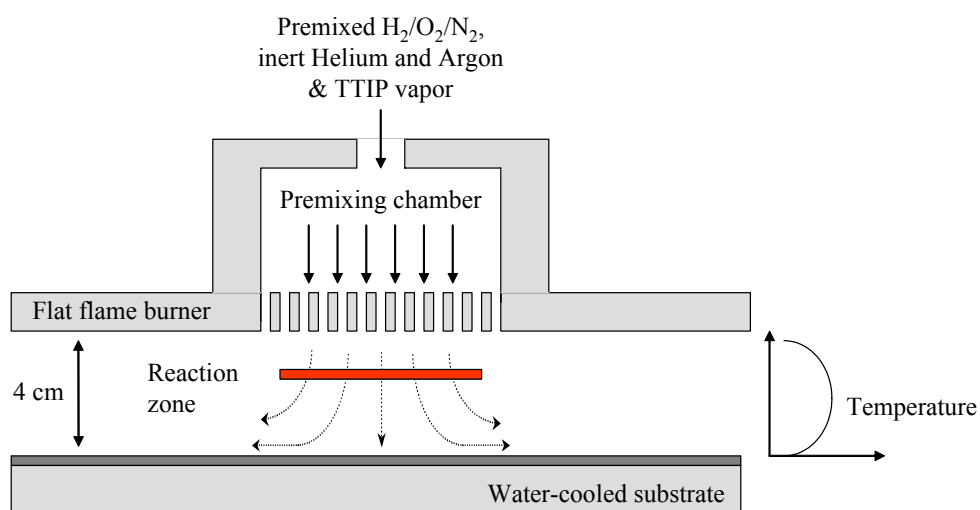


Figure 3.4. Premixed flame setup.

Vaporized precursor is entrained in a carrier gas and mixes with the combustible gases, diluent, and inert gases in the mixing chamber above the burner plate. Pyrolyzed precursor vapor generates radicals which are then oxidized and nucleate into nanoparticles. All gas flows are controlled by either Aalborg or Brooks mass flow

controllers (MFCs). Stainless steel, 1/4-inch diameter tubing is used for almost all plumbing of gas lines into the chamber. Lines responsible for carrying precursor vapor are 3/8-inch diameter and are heated to and temperature-controlled at 140-150°C in order to prevent precursor condensation in the lines.

3.1.3 Precursor delivery unit

Titanium (IV) tetra-isopropoxide (Acros Organics, Titan(IV)-isopropylat, 98+%) is used as the metal-organic liquid precursor for synthesizing nano-TiO₂. The liquid precursor is placed in a glass bubbler and connected to the delivery lines with a standard o-ring vacuum connection. A circular cross-section radiant heater is placed around the bubbler and is used to heat the precursor. A 12-inch long K-type thermocouple is inserted into the bubbler and the temperature is maintained at 85°C by a Yokogawa UT37 temperature controller. During experimental runs, it is very important to monitor the bubbler temperature and ensure that it stays roughly between 84-88°C so that precursor loading rate is constant. The flame is seeded with precursor by entraining the precursor vapor in H₂ gas. The carrier gas flow rate is controlled by a Brooks mass flow controller. A check valve is located just downstream of the mass flow controller in order to prevent any backflow of vaporized precursor into the controller that could potentially cause damage.

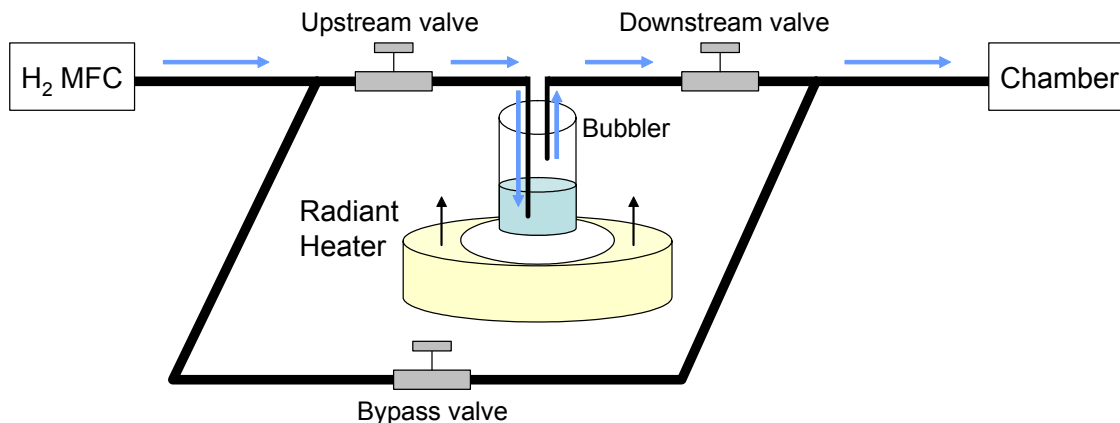


Figure 3.5. Precursor delivery setup with three-valve system and radiant heater.

A three valve system, depicted in [Figure 3.5](#), is used around the precursor bubbler. One valve is located upstream of the bubbler, one downstream, and one on a bypass line around the bubbler. All three valves are high-temperature ball valves. All delivery lines are made of stainless steel. The pipe diameters are $\frac{1}{4}$ -inch before the bubbler and along the bypass line and all other tubing that delivers the precursor vapor is then $\frac{3}{8}$ -inch after the bubbler. This larger diameter tubing after the bubbler is used to prevent precursor condensation and build up during irregular starts and stops of the experiment or during abandoned runs. In addition, all stainless steel delivery lines that carry precursor vapor are resistively heated with heater ropes and temperature-controlled to 30°C or more above the bubbler temperature in order to prevent precursor condensation. The bypass valve is left open during flame ignition. After the flame is ignited, the valve downstream the bubbler is opened; then the valve upstream is opened, and then the bypass valve is closed. This order is very important as it prevents unwanted back flow of precursor vapor into the mass flow controller. During shutdown, the valve combination operation is simply

reversed. The bypass will be opened first; then the upstream valve is closed, and then the downstream valve is closed.

3.1.4 Water-cooled substrate

The water-cooled substrate serves a variety of purposes. It establishes a stagnation point flow field, allowing simplicity in modeling. It presents a strong temperature gradient, driving supersaturation so that nanoparticles may homogeneously nucleate, mature, and then exit the reaction zone of the flame. Finally, the cold substrate induces deposition of the nanoparticles by means of a strong thermophoretic force generated by the steep temperature gradient in the boundary layer.

There are two main parts to the water-cooled substrate: a thicker bottom piece and a thinner plate on top that is in good thermal contact. The dimensions of these plates are 5.5" x 6". The thicker aluminum plate below has channels machined out for the cooling water to enter and then exit and cycle back to a temperature-controlled water bath. The thinner stainless steel plate on the top is securely fastened down by four (4) screws located on the corners that go completely through both the thicker and thinner parts of the substrate. The water bath temperature is set to 20°C, which is above the boiling point for the operating pressure, in all experiments to ensure that water condensation does not form on the substrate. In the event of water condensation, the collected powders would have a considerable amount of water adsorbed via chemisorption over the large surface area of the particles. This would encourage particle agglomeration and cause difficulties with ex-situ powder characterization.

A small 3" square plate is used to cover the center area of the substrate directly below the flame. This cover plate prevents particle deposition on a selected area of the substrate

during the initial stabilization of the flame. Once the flame, bubbler temperature, and precursor delivery lines have all reached their stable state, the cover plate is removed. There is a thin vertical screw (length less than the 4cm gap between substrate and burner) that facilitates the removal of the cover plate. The igniter arm is temporarily brought into the flame zone and is used to quickly knock the cover plate off of the substrate. Only particles formed in the stable flame with uniform precursor loading are collected for samples and characterized.

3.1.5 Pressure control system

A single-stage Sogevac SV40 rotary vane vacuum pump, a digital MKS PDR2000 dual capacitance manometer, and a high-vacuum valve on the lid of the chamber have been used to monitor the chamber pressure during experimental runs. The pressure has been kept to ± 1 torr of the experimental pressure parameter. Some precautions have been taken in order to protect the mechanical components of the vacuum pump. Concerns arise due to the hardness of the synthesized ceramic nanopowders and the potential damage that they might cause inside of the pump. A liquid nitrogen trap is located between the high-vacuum valve on the lid of the chamber and the vacuum pump. Four (4) liters of liquid nitrogen are used each time the experiment is run. Typically, the nitrogen trap is filled every fifteen (15) minutes. The trap is responsible for capturing water generated as a byproduct of the hydrogen combustion process and any nanoparticles that are pumped out of the chamber as an aerosol. Some other preventive measures were used but were found to be unsuccessful. Different combinations of a stainless steel mesh and a nylon mesh were installed in different locations of the vacuum tubing from the chamber to the pump, but did not yield favorable results. Typically, the vacuum pump lost suction in as little

time as twenty (20) minutes. This is a result of the constriction in the tubing from the mesh installations. Since the duration of one run is between forty (40) and fifty (50) minutes, the meshes were removed and only the liquid nitrogen trap is employed to protect the vacuum pump.

3.1.6 Synthesis chamber

The low-pressure chamber is a double-walled stainless steel cylinder which is 470cm in diameter. The chamber is operated at 20, 30, or 40torr and the pressure is controlled as described previously. An absolute pressure gauge is mounted on the sidewall of the chamber and is used as a secondary pressure readout to monitor the experiment during runs. A pressure release valve is located on the wall of the chamber and is used for re-pressurizing the chamber when necessary. The burner and substrate are mounted by supporting arms on two long vertical screws. This allows for the height of the burner and substrate both to be adjusted to a desired gap distance. The two vertical screws are attached to a disk at the bottom of the chamber. The chamber has three (3) orthogonal ports complete with quartz windows for optical access and one (1) more orthogonal port with several feedthroughs for access into the chamber. The optical ports are well suited to accommodate the various laser-based diagnostic arrangements that can be employed. The entire chamber rests on a three-axis positioner to aid in spatial probing of the flame structure by a fixed laser excitation beam and collection optics.

3.2 Operating parameters and procedure

All experiments are run using premixed $H_2/O_2/N_2$ /inert(s) (H_2 /Airgas/ultra high purity, O_2 /Airgas/ultra high purity, N_2 /Airgas/ultra high purity). The flames burn with an

equivalence ratio of roughly 0.42, low-pressure environments of 20, 30, or 40torr, and a substrate-burner gap of 4cm. The following is the standard operating procedure for the experiment:

- (1) Turn on the exhaust fan, and turn on the vacuum pump. Pump the chamber down *slowly* to 1-2torr, and check the chamber leakage rate;
- (2) Close the vacuum pump valve, and then flow N₂ into the chamber and bring the pressure up to a few torr less than the experimental operating pressure for the case being run (i.e. 17-18torr, 27-28torr, or 37-38torr);
- (3) Open the valve immediately downstream of the bubbler to equalize the bubbler pressure with the chamber pressure, and then re-close it;
- (4) Turn on the temperature controller to bring the bubbler temperature to the set point (85°C), then wait for bubbler to get to ~70°C, and then turn on the other temperature controllers for the delivery lines (140-150°C);
- (5) Turn water valve on at the wall, and then switch on the water baths, and bring the temperatures of the burner (80°C), substrate (20°C), and chamber walls (25°C) to their set points – this part will take some time and can be done immediately following step (4);
- (6) When all of the temperatures (including the bubbler, lines, burner, and substrate) become stable, the flame is ready to be ignited;
- (7) Pour one liter of liquid nitrogen into the nitrogen trap to capture the condensable particles and to protect the vacuum pump from contamination;

- (8) Open valves downstream from the mass flow controllers (MFCs) and valves upstream of the Aalborg controllers controlled by the command module;
- (9) Open upstream ball valves of the Brooks controllers and immediately open MFCs simultaneously by hitting <ESC> and then <AUTO> on the command module;
- (10) Bring igniter into flame, turn Variac power supply to 25% of 120V and wait for the flame to ignite;
- (11) After the flame ignites, rotate the igniter out of the flame zone, and quickly open the high-vacuum valve on the lid of the chamber to relieve the pressure build up;
- (12) Monitor the chamber pressure with the gauges and make small adjustments with the high-vacuum valve until the pressure in the chamber is more or less constant. Fine adjustments will be made throughout the duration of the run;
- (13) *Slowly* and cautiously open the valve immediately downstream of the bubbler (continually checking inside the chamber, being careful not to quench the flame by opening the valve quickly);
- (14) *Slowly* open the valve immediately upstream of the bubbler, and then carefully close the bypass valve;
- (15) After the precursor-loaded flame becomes stable, use the igniter arm to knock the cover plate off the substrate, allowing particles to deposit on the substrate (where the powder sample will be collected from);
- (16) Run the experiment for 30-50 minutes, remembering to re-fill the liquid nitrogen trap with roughly 1 liter for every 15 minutes of operation;

- (17) When it is time to shut down, open the bubbler bypass valve; close the upstream valve; and then close the downstream valve (in this specific order to protect the mass flow transducers from reverse flow contamination);
- (18) Close the fuel and oxidizer, and allow nitrogen to flow for about 20 minutes to carry off precursor residue;
- (19) While nitrogen is running, turn off the bubbler temperature controller, and set the water baths to room temperature for active cooling;
- (20) After nitrogen purge is finished, close nitrogen tank, and turn off precursor delivery line temperature controllers;
- (21) Turn off the water baths and close the water valve at the wall;
- (22) Turn off the vacuum pump and the roof exhaust fan.

3.3 Ex-situ characterization methods applied

Several pieces of equipment have been used for particle characterization and are described in the following subsections. Important characteristics that have been obtained include aggregate particle size, specific surface area, primary particle size, particle morphology, crystallinity, and phase composition.

3.3.1 Brunauer-Emmet-Teller (BET)

BET is a well-known method utilizing gas adsorption on a solid surface to measure specific surface area. This method depends on the fact that at a given pressure, a certain amount of adsorbate (gas) will form a layer over the adsorbent (solid). The equipment used in this work (Micromeritics Gemini 2375) applies a volumetric method. The

pressure, volume, and temperature of an adsorbate are measured, and then the adsorbate is brought into contact with an absorbent. When the system reaches equilibrium, the amount of gas is then calculated again and the difference in free gas represents the adsorbate lost from the gas phase to an adsorbed phase on the surface of the powders.¹³ The multi-point BET nitrogen absorption at liquid nitrogen temperature is a commonly applied method. A graph of the amount adsorbed (V , volume) at a constant temperature (T , liquid nitrogen) verses the adsorption pressure (P , pressure) constitutes an adsorption isotherm.¹³ In this work, a relative pressure has been used where the adsorption pressure is normalized by the saturation vapor pressure in the equipment laboratory on the day of testing.

By means of the BET equation, the measurement of the adsorbed gas can be used to determine the gas volume adsorbate on the particles. This allows for the calculation of the specific surface area of the nanopowder sample. From the specific surface area, the equivalent primary particle size is calculated by:

$$d_{BET} = \frac{6}{\rho \cdot SSA} \quad (3.1)$$

where:

ρ : density of the powder (3.840 g/m³ for TiO₂)

SSA: specific surface area generated by the BET equation.

Although heavier samples are preferred, typical samples characterized in this work are less than 0.05g. Samples are degassed for two (2) or more hours at temperatures ranging from 70-100°C. Five (5) or six (6) measurement points are used, and the recommended evacuation rate of 300mmHg/min is applied. After characterization, the sample tubes

with powders are dried in an oven and then the powders are returned to their original container. BET bulb sample tubes are then cleaned with alcohol and distilled water, sonicated, and dried overnight in an oven.

3.3.2 X-Ray Diffraction (XRD)

This method of characterization can be used to identify crystalline phases in powder or even film samples. The term crystalline simply means the degree of structural order in a solid where atoms or molecules are arranged in a periodic manner in a unit cell which itself is much larger than the atoms or molecules that it contains. The XRD technique involves the detection of characteristic X-rays produced by bombarding a solid sample with high-energy electrons. This method can be easily used to gather qualitative and quantitative information regarding the sample.

The XRD equipment and analysis software collect a spectrum and allow a search through a database in order to identify the phases present in the sample by noting relative peak heights and locations. Information about the lattice spacing and the structure of the crystalline unit cell can be derived since the diffraction occurs according to Bragg's Law, which relates lattice spacing to X-ray wavelength.

MDI Jade software is used for data processing and analysis. The software package is capable of quantitative analysis, giving information regarding the crystalline phase compositions. A Siemens D500 X-ray Diffractometer is used in this work to verify phase composition and gather quantitative information regarding those phases. Samples are

prepared in a small aluminum sample holder with a shallow oval-shaped cutout or affixed on a custom made glass slide by means of vacuum grease or double-sided tape.

Chapter 4

Computational Modeling

In this body of work, a modified Sandia SPIN code is used to simulate the gas-phase flame structure. The SPIN code assumes a one-dimensional stagnation point flow and stores the flow field characteristics in a database. Using the flame structure database generated by the SPIN code, the particle growth and evolution can be forecast by the monodisperse and sectional models. Essentially, the goal is to model the entire synthesis process so that accurate predictions of the products can be achieved. Accurate predictions of particle growth and evolution can allow for scale-up of the synthesis process from the laboratory into industry. The union of the experimental results and computational modeling provide the unique opportunity to tailor the synthesis process in order to manufacture the most desirable powders.

Complex physical and chemical phenomena are involved in the process of synthesizing nanopowders such as TiO_2 . The computational models applied for particle growth should obviously capture the most relevant and important phenomena that affect the evolution of the particle during the course of the experiment. Of primary concern are the interactions between the particles themselves, the interactions between the particles and the surrounding gas-phase environment, and the particle transport through the flow field. This chapter describes the flame structure simulation by the Sandia SPIN code and goes

into the basics of the monodisperse and sectional models that are used to simulate the particle growth and evolution.

4.1 Flame Structure

It is a well-known fact that the gas-phase temperature history plays a key role in particle evolution in the flame synthesis of nanoparticles. In order to predict particle growth, a robust simulation is needed to map out the temperature history of the particles in the flame as well as the gas-phase velocity flow field throughout the gap between the burner and the substrate. The simulations of the flame structure in this work have been done with the Sandia SPIN code. This code assumes a one-dimensional stagnation flow and is a very reasonable model for the flat flame used in the experimental work found in this thesis. Previous work has applied laser-based diagnostics such as laser-induced fluorescence (LIF) to map OH radical concentrations and gas-phase temperature distributions along the axial centerline of the flame, with excellent agreement with the simulations from the Sandia SPIN code.²²

The SPIN code is intended to model a steady-state, one-dimensional, rotating disk/stagnation flow chemical vapor deposition (CVD) reactor.¹⁴ For the experimental setup used in this work, this SPIN code can be adapted for our purposes by applying a zero-rotation rate and the appropriate boundary conditions at the substrate. The problem is described as an infinite solid stationary disk separated from a facing parallel porous surface at a distance of $x=L$. The flow at $x=L$ represents the inlet flow conditions. A diagram of the described conditions can be seen in [Figure 4.1](#). The SPIN code uses fluid flow and chemistry models to determine the flow field and transport properties between

the burner plate and the substrate as well as the chemical reactions occurring in the gas-phase.

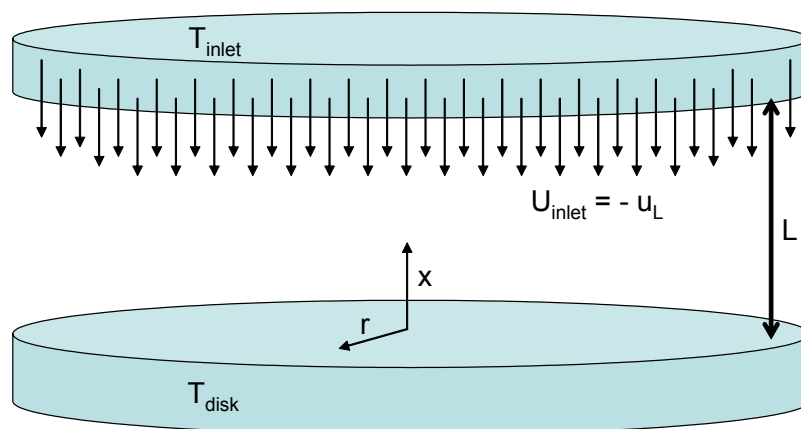


Figure 4.1. Schematic of the infinite-radius substrate and inlet boundary conditions used by the modified Sandia SPIN code.

The SPIN code utilizes a modular structure where the final SPIN code calls on data generated in the CHEMKIN utility package. The CHEMKIN package provides the necessary chemical kinetic, thermodynamic, and transport parameters. Input directly from the user is used alongside the CHEMKIN gas-phase, SURFACE CHEMKIN, and TRANSPORT packages to find a solution for the flame structure. A flow chart depicting the relationship of the SPIN code to the CHEMKIN utility package modules can be seen in Figure 4.2. The three preprocessors must be run in the following order: CHEMKIN, SURFACE CHEMKIN, and then TRANSPORT. After the successful completion of these three preprocessors, the SPIN code can be run. A keyword input format is used to provide SPIN with the particular parameters of the reacting flow problem at hand. From the keyword input and the information gathered from the CHEMKIN utility package, a

solution can be found. It is, of course, possible to find a new solution from scratch, but it is often more efficient to start with a previously solved flame structure by using a restart file.

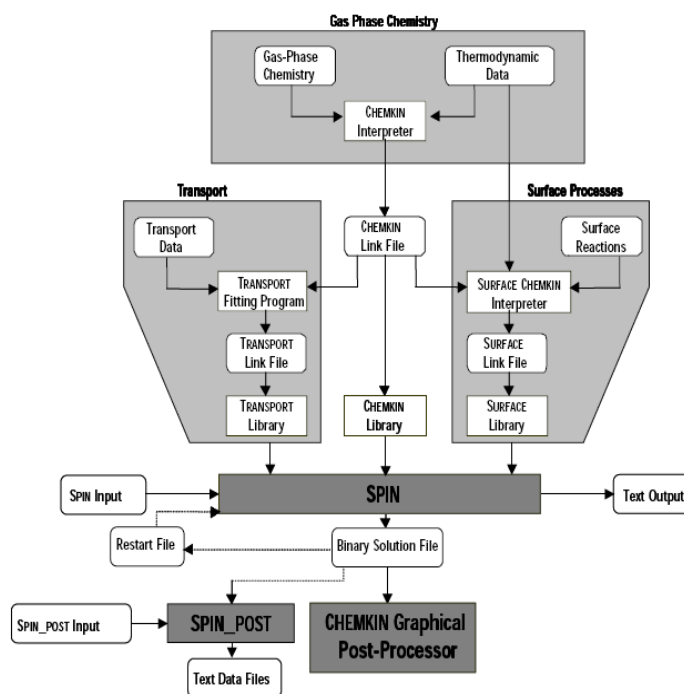


Figure 4.2. Relationship of the SPIN program to the CHEMKIN, SURFACE CHEMKIN, and TRANSPORT modules.

The boundary conditions applied are the following:

- (1) Inlet mass flux and temperature at burner;
- (2) No-slip and constant temperature at substrate;
- (3) Recombination of H, O, OH, and HO₂ with unit sticking probability at the substrate;

- (4) Gas-phase mass flux of each species balanced by creation or depletion of that species by surface reactions.

The governing equations in the SPIN code are solved using TWOPNT which applies a hybrid Newton/time-step algorithm. The ordinary differential equation boundary value problem is simplified into a system of algebraic equations. The first solution is found using a coarse mesh, and more mesh points can be added to make finer grids by interpolating the solution on the coarse mesh. The solution can be refined as many times as necessary to the satisfaction of the user. There are three major subroutines that are applied by TWOPNT in solving the governing equations. These subroutines include NEWTON which applied Newton's method in an effort to solve the boundary value problem, TIMSTP which begins time-stepping if Newton's method fails, and REFINE which is responsible for adapting the mesh.

Since SPIN depends on an iterative process in finding solutions, it is necessary for the user to give a starting estimate of the solution. The initial guess can have as few as only five (5) or six (6) grid points. Thereafter, the user has control of keyword parameters GRAD and CURV. GRAD is an adaptive mesh parameter that controls the number of grid points inserted into regions of steep gradient. CURV is an adaptive mesh parameter that controls the number of grid points inserted into regions of high curvature. As the values of GRAD and CURV decrease, the accuracy of the solution increases. For simulations used in this thesis, GRAD and CURV values of 0.02 are used. These typically generate meshes with just over one thousand (1,000) grid points.

4.2 Particle Growth and Evolution

There are an abundance of both physical and chemical phenomena that affect particle growth and evolution. In this work, as in many others, the nanoparticles are derived from the gas phase of a liquid precursor. As a result of this, consideration must be given to the gas phase chemistry, particle nucleation, particle growth, and particle transport. Particle growth itself has many facets including coagulation, coalescence, as well as surface growth via evaporation and condensation. Brief descriptions of each of these are given in this section.

The liquid precursor selected for the synthesis process is initially heated outside the chamber into the gas-phase in a closed system. Sweeping hydrogen gas carries the precursor vapor into the premixing chamber and then into the flame zone. As a result of the high temperatures in the flame, the vapor precursor decomposes readily into radicals. In the flame, these radicals chemically evolve into oxide monomers and/or clusters. The flame temperature is actually too cold to harbor these species any longer and they will homogeneously nucleate into nanoparticles without the aid of any foreign surfaces. This is solely the result of the supersaturated state of the flame. The initial particle sizes are represented by a critical size and will fall into a narrow size distribution. After the nucleation of these particles, they continue to grow in the flame while experiencing particle-to-particle collisions leading to coagulation and coalescence, as they interact with the gas-phase combustion environment around them, and even as they experience the evaporation and condensation of monomers on their surfaces. These basic steps are visually represented in [Figure 4.3](#).

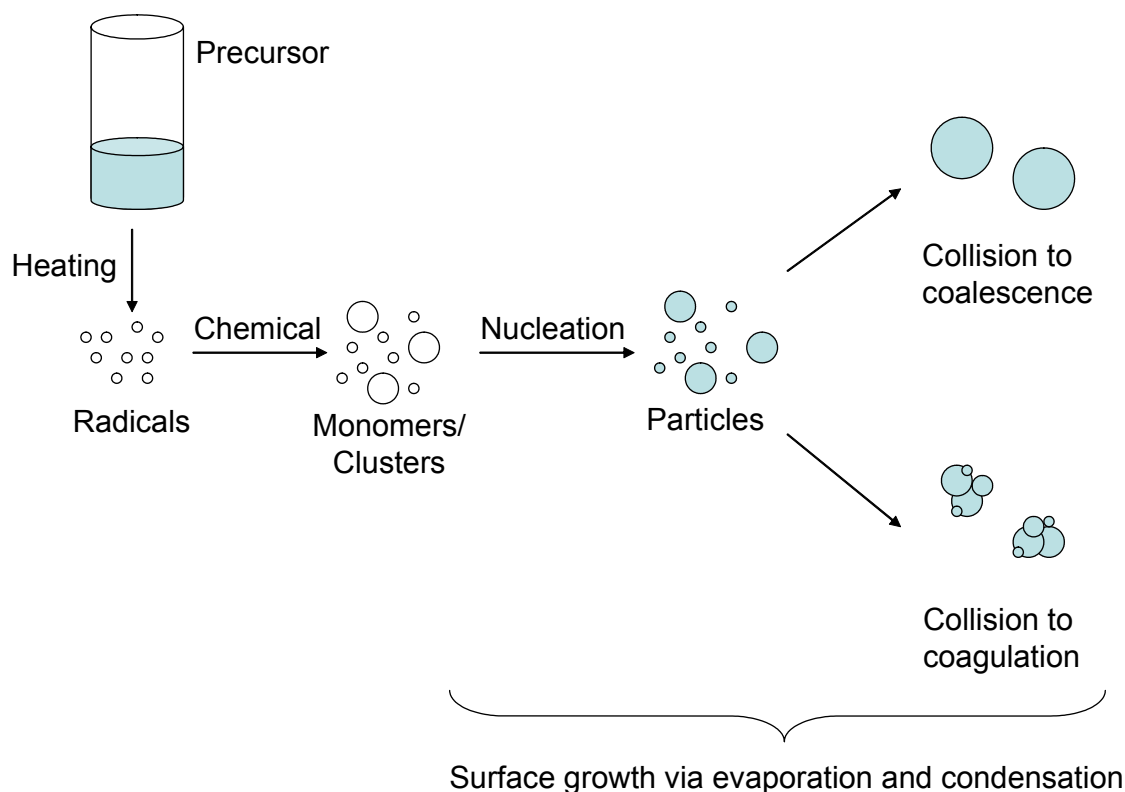


Figure 4.3. Basic flow diagram showing steps in particle formation and growth during flame synthesis processes.

A variety of models exist for the simulation of particle growth and evolution. These models vary in their complexity and two of them have been chosen and applied in this thesis. The monodisperse model neglects the polydispersity of the particles, as the name suggests. Primary and aggregate particle sizes are calculated while only coagulation and coalescence are taken into account. The more robust sectional model takes into consideration precursor decomposition, particle nucleation, coagulation, coalescence, and surface growth. Among other parameters, the sectional model reports primary and aggregate particle sizes and geometric standard deviation.

4.2.1 Precursor decomposition and particle nucleation

The precursor vapor carried into the flame by the sweeping gas becomes thermally decomposed in the high temperatures of the flame. With the help of excess oxygen from a lean flame, these radicals readily form titanium oxide vapors. Hydrolysis is another means of generating titanium oxide vapors in the flame. As previously mentioned, the supersaturation of the flame will cause the titanium oxide vapors to nucleate into stable nuclei that will grow into TiO_2 particles. For the sake of the particle growth and evolution models, a critical cluster size is assumed. Only clusters of monomers above this critical size are assumed to form stable nuclei that will continue to grow.

4.2.2 Coagulation

Coagulation involves two or more particles joining together and sharing a connecting point on their surfaces. A simple depiction of this can be seen in [Figure 4.4](#).



Figure 4.4. Coagulation process.

The random movement of particles in a liquid or gas suspension is caused by numerous collisions between the liquid or gas molecules with the surface of the particles. This random movement is called Brownian motion and is accepted as being the dominant mechanism behind coagulation of particles in the sub-micron range. A collision frequency function to aid in modeling the coagulation process can be determined and

depends on many factors including the diffusion coefficient of the particles as well as their density, volume, shape factor, and diameter.

4.2.3 Coalescence

Under high temperatures, coagulated particles will proceed to undergo coalescence. Coalescence is the fusing together of two or more particles into one particle of larger diameter. A simple diagram of this process is seen in [Figure 4.5](#).



[Figure 4.5](#). Coalescence process.

As two or more particles fuse into one single particle, the density is assumed to remain unchanged. During the coalescence process, it is noted that the total volume has not changed, but rather only the surface area has changed. As Brownian motion is considered to be the driving force behind particle collisions leading to coagulation, then coalescence is simply the effort of minimizing the surface energy of the particles. With coalescence, the surface area of the final particle will be less than the sum of the original primary particles that make it up.

4.2.4 Surface growth

Two things are meant by the term surface growth: one is based on condensation and the other on evaporation. As alluded to earlier, the gas-phase precursor lends itself to nucleating into monomers. Generally speaking, this nucleation will happen due to the

supersaturation of the flame with the gas-phase precursor and the process requires no foreign surface. That is not to say that, if present, a foreign surface could not act heterogeneously as a nucleation site. This is actually the very case that represents the condensation part of the surface growth process.



Figure 4.6. Surface growth via condensation process. **Figure 4.7.** Surface growth via evaporation process.

The condensation of monomers on an existing particle surface is shown above in [Figure 4.6](#). Sometimes, however, the monomers on the surfaces of the particles can evaporate off of the particle. This is shown simply in [Figure 4.7](#). The simultaneous processes of evaporation and condensation make up the surface growth of the synthesized particles.

4.3 Monodisperse Model

The monodisperse model is a simple representation of the particle growth and evolution. A model developed primarily by Kruis and Pratsinis is used here.¹⁵ This model neglects the polydispersity of the aggregate and primary particles. While the simulation is perhaps not as accurate as other more robust models that are available, it is well-simplified, solutions are readily found, and it is computationally time-efficient. The monodisperse model serves well as a first approximation and can give one the ability to make some general conclusions and predictions for particles produced under any given set of flame

conditions. One noteworthy feature of the monodisperse model is its ability to be coupled with the SPIN code flame structure simulation.

Particle and aggregate motion in the flame results from forces such as Stokes drag force and the thermophoretic force. As these particles and aggregates move through the flame, their collisions with each other cause the coagulation and coalescence that is described earlier. The monodisperse model describes the progress of the aggregate particle number concentration, volume, and surface area. Both coagulation and coalescence are taken into consideration with this model.

The monodisperse model is also capable of generating information regarding the primary particle sizes and numbers found in an aggregate. The diameter of the primary particle is quite simply defined as the ratio of the aggregate volume to its total surface area:

$$d_p = \frac{6v_a}{a_a} \quad (4.1)$$

It is noted that this relation will not take into account any coalescence effects that cause a decrease in surface area. The number of primary particles is simply calculated by dividing the aggregate volume by the volume of a monodisperse primary particle:

$$n_p = \frac{v_a}{v_p} \quad (4.2)$$

The monodisperse model applied in this work takes on several assumptions that essentially turn it into a 1-D model along the axial centerline of the flame:

- (1) the precursor decays instantaneously at a fixed temperature of 800K¹⁶;
- (2) homogeneous nucleation of particles occurs at a critical size of 0.4nm;
- (3) particle velocity is the same as the corresponding gas-phase velocity at the location of instantaneous homogeneous nucleation;
- (4) only a negligible difference exists in time and temperature histories of particles nucleating at different distances from the centerline.

The monodisperse model also uses a collision frequency function which takes the particle shape and its accessible surface area into consideration. The logarithmic expression shown below is used which incorporates the surface area and volume of the aggregate particles.

$$factorAF = 1 - 0.03(\alpha/\beta) \log\left(\frac{[YY(2)]^3}{36\pi[YY(3)]^2}\right) \quad (4.3)$$

where:

α : constant

β : constant

YY(2) : particle surface area (m²)

YY(3) : particle volume (m³)

The initial particle concentration when precursor decomposition occurs is estimated from the precursor-loading rate and the total volume flow rates of the premixed gases. The nano-TiO₂ is assumed to have a density of 3.84x10³ kg/m³, which is the bulk density of titania.

4.4 Sectional Model

The sectional model is a more realistic means of modeling the particle growth and evolution. A number of sections span the possible size range of the particles. The sectional model can be applied in a zero-order or in a high-order fashion. The zero-order model will assume a monodispersity of particles in each individual section. High-order sectional models will commonly apply a low-order polynomial function to the particle size distributions within each individual section. These high-order versions should obviously generate more accurate results but suffer from instabilities. However, given a sufficient number of sections, very good results can be obtained from the zero-order version assuming monodispersity within each section.

In addition to zero-order and high-order options with the sectional model, there is also a possibility of using a one-dimensional or two-dimensional model. In the 1-D model, only one internal coordinate is necessary for defining the sections. In choosing volume or mass, the assumption is made that coalescence occurs instantaneously and that all particles are spherical in shape. On the other hand, the 2-D model will utilize two internal coordinates for each section while defining each section by surface area and volume. Instead of using the computationally expensive 2-D model, a modified 1-D model is used here.^{17,18} It is not necessary for all particles to be exactly spherical in shape, as an average surface area is used. This is how coalescence is taken into consideration. In this work, a zero-order and one-dimensional model is applied.

The model used in this work was adapted previously from the work of Prakash *et al.*¹⁹ Size sections are defined by volume; monodisperse particles are assumed within individual sections, and particles do not have to be fully coalesced as an average surface area is used within each volume section.^{17,18} For all sectional models applied in this work, 102 volume sections at a geometric spacing factor of $q=1.2$ on a logarithmic volume scale are used. For the population balance of each section, precursor decomposition, particle homogeneous nucleation, coagulation, coalescence, and surface growth via evaporation and condensation are all taken into account. Similar to the monodisperse model described in the last section, a starting diameter of 0.4nm is assumed for TiO₂ nanoparticles. The free molecular regime is assumed for this model. This regime is for Knudsen numbers greater than ten (10) as defined by the ratio of the characteristic mean free path of the gas to the particle radius.

4.5 Particle transport and external forces

In these simulations, a Lagrangian approach is taken for numerical simulation of the nanoparticle dynamics. The velocity of the particles is calculated taking into consideration Stokes viscous drag and the thermophoretic force. An adaptive fourth-order Runge-Kutta method is used to interpolate the results of the SPIN code and to re-map the local property information for the particle growth and evolution modeling.

The thermophoretic force plays a significant role in particle transport. This is a common phenomenon where small particles in an aerosol will experience a force when in the presence of temperature gradients. This force will direct the particle in the direction of the lower temperature. It is thought that this force is a result of the atoms and molecules

in the higher temperature region having greater momentum as they bombard the particles in the aerosol. These stronger hits from molecules in the higher temperature zone will cause a net force in the direction of the lower temperature where the molecules have less momentum. The thermophoretic force is considered to be a major factor in flame synthesis of nanoparticles as the temperatures are high and the gradients are extremely steep through narrow reaction zones. This force can cause a backward migration of particles toward the cooled burner or, at a further axial distance, a push towards the substrate. As a matter of fact, the thermophoretic force has a great deal to do with the collection of the nanoparticles on the substrate. As mentioned in Chapter 3, the substrate is water-cooled. Consequently, particles experience an extremely strong thermophoretic force and drift velocities downwards towards the cool substrate once they are within the thermal boundary layer.

4.6 Coupling of flow field, particle transport, and particle growth

The flow field information including the temperature, gas velocities, viscosity, and density are all obtained by the SPIN simulation discussed earlier in the chapter. This data is saved in a descriptive flow field database. Due to the nature of the database and the particle growth models, data for the exact location of the particle during the simulation is likely unavailable. In this case, a seven-point polynomial interpolation is performed between points in the flow field database. The procedure for the calculation of particle trajectories in the models is:

- (1) Read flow field database into large matrices, and read initial conditions including monomer number concentration, monomer diameter, nanoparticle surface tension, and vapor pressure;
- (2) For any given integration step Δt , solve for Δx and local velocity using the adaptive fourth-order Runge-Kutta;
- (3) Calculate temperature, gas velocity, viscosity, and density by interpolation at the current position from flow field database;
- (4) For the given integration step Δt , determine the particle size and particle number concentration by solving simplified gas dynamic equations;
- (5) Update particle diameter, and continue on with next integration step Δt ;
- (6) Continue process from step (2) until particles have reached the substrate.

Chapter 5

Standard Flame Synthesis Conditions

The previous chapters have outlined the purpose of this study, and the next chapters will present the information gathered from the flame structure simulation, particle growth models, and corresponding experiments. Three standard cases at three different pressures (20, 30, and 40torr) are presented in this chapter. The flames involved are all hydrogen-oxygen flames with nitrogen dilution. The 20torr standard case (20torrSTD) has $\text{H}_2/\text{O}_2/\text{N}_2$ ratios of 1.0:1.213:0.7377, a mass-flux at the burner of 2.519 mg/s/cm^2 , and a precursor-loading rate of $6.452 \times 10^{-4} \text{ mol/min}$. The 30torr standard case (30torrSTD) has $\text{H}_2/\text{O}_2/\text{N}_2$ ratios of 1.0:1.213:2.0428, a mass-flux at the burner of 3.064 mg/s/cm^2 , and a precursor-loading rate of $4.73 \times 10^{-4} \text{ mol/min}$. The 40torr standard case (40torrSTD) has $\text{H}_2/\text{O}_2/\text{N}_2$ ratios of 1.0:1.213:3.05615, a mass-flux at the burner of 3.480 mg/s/cm^2 , and a precursor-loading rate of $3.87 \times 10^{-4} \text{ mol/min}$.

The flame structure simulations are done using the SPIN code, and the flow field database is inputted into the monodisperse and sectional models to calculate particle growth and evolution. Comparisons of the particle growth models with actual *ex-situ* characterization of the product will be presented in this Chapter 5. Powder samples are characterized using the XRD and BET methods, as described earlier, to determine particle phase and crystallinity, specific surface area, and primary particle size. These cases serve as a baseline for comparison with the results presented in the following two chapters.

5.1 Flame structure simulations of the standard cases

As detailed in Chapter 4, the SPIN code is used to simulate the flame structure of the three standard cases with the parameters tabulated below in [Table 5.1](#). Each case has an equivalence ratio of 0.42. A lean flame is used because the excess oxygen is useful for synthesizing the oxide powders. A low-pressure environment is utilized to aid in minimizing the effect of molecules in the atmosphere as they would tend to strike the nanoparticles and create more collisions that lead to coagulation and coalescence. Additionally, the low-pressure environment helps to reduce particle residence times which will prevent unnecessary particle growth and evolution resulting from longer times spent in the hot flame zone.

H ₂ /O ₂ ($\phi=0.42$)	H ₂	O ₂	N ₂	Inlet gas velocity (cm/s)	Mass flux (mg/s/cm ²)	Precursor-loading rate (mol/min)
20torrSTD	1.0	1.213	0.7377	150	2.519	6.45 E-4
30torrSTD	1.0	1.213	2.0428	110	3.064	4.73 E-4
40torrSTD	1.0	1.213	3.05615	90	3.480	3.87 E-4

Table 5.1. Experimental parameters for the standard flame synthesis cases.

[Figure 5.1](#) and [Figure 5.2](#) show the temperature history of the three standard cases and also the gas-phase velocity profiles of the flame under the given conditions. As can be seen, the temperature profiles are the same for all cases via strategic dilution. The 0cm mark indicates the substrate and the 4cm mark is the burner exit. Over the course of the 4cm gap, a maximum temperature of roughly 1600K is achieved near the 1.6cm mark. For the velocity profiles, the cold-gas inlet velocities are different. The 20torrSTD case starts at 150cm/s, the 30torrSTD at 110cm/s, and the 40torrSTD at 90cm/s. The shape of

each of the gas-phase velocity profiles is similar, but the much faster 20torrSTD velocities result in shorter residence times for the particles at that pressure. These cases allow us to isolate the effect of residence time from that of temperature.

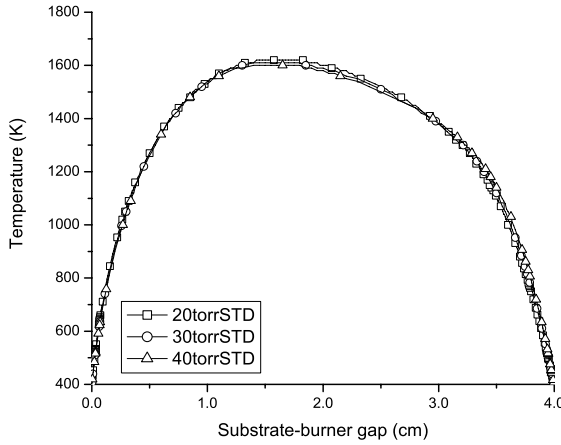


Figure 5.1. Temperature profile with respect to gap distance for the standard synthesis conditions.

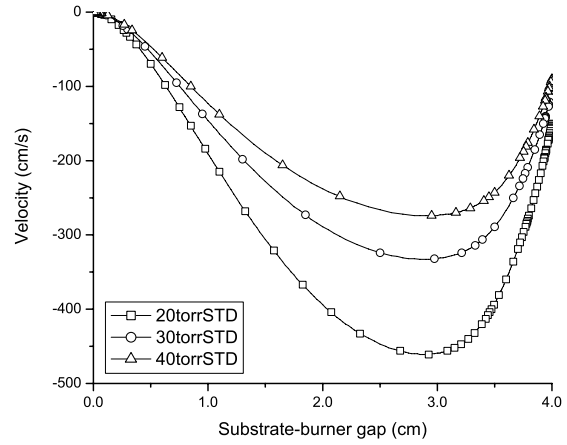


Figure 5.2. Velocity profiles with respect to gap distance for the standard synthesis conditions.

5.2 Monodisperse model simulations of the standard cases

A monodisperse model for particle growth is employed to track the evolution of the primary and aggregate particle sizes. The flow field database generated by the SPIN code is inputted as described earlier. The results of this model are seen in [Figure 5.3](#) and [Figure 5.4](#) below. In order to account for different behaviors of aggregate development, a particle shape factor is incorporated into the model. As shown in Eq. (4.3), a logarithmic expression is used which incorporates the surface area and volume of the aggregate particles. In all of the standard cases presented in this chapter, α and β constants are chosen to be 8.5 and 6.0, respectively. These values lead to reasonable final particle sizes and smooth growth curves.

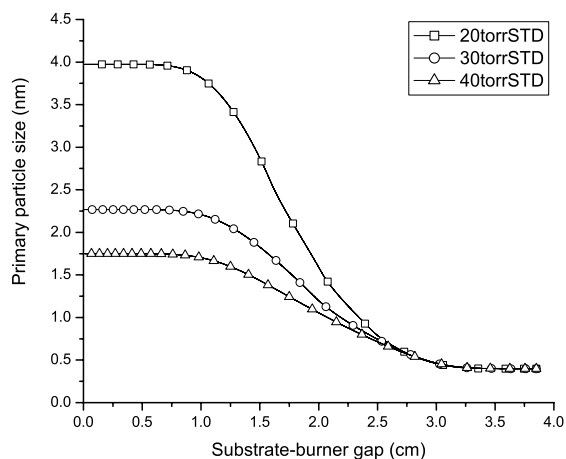


Figure 5.3. Primary particle size with respect to gap distance for the standard cases as calculated by the monodisperse model.

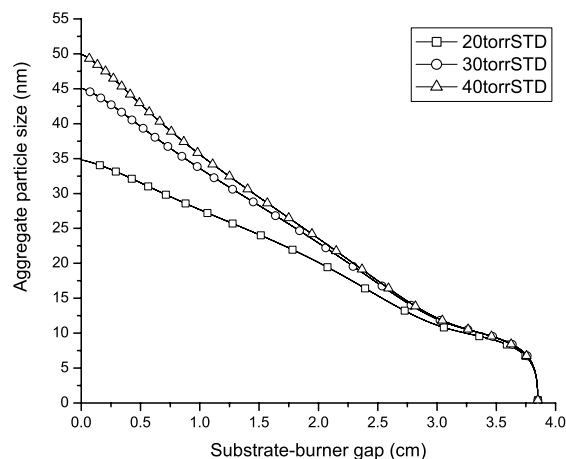


Figure 5.4. Aggregate particle size with respect to gap distance for the standard cases as calculated by the monodisperse model.

The primary particle growth starts with an initial particle size of 0.4nm and begins its trajectory at the 3.85cm mark. After a short period of slow development, the particles enter the hot zone of the flame and experience a quick rise in primary particle size. The primary particles then tend to reach a plateau near the 1.0cm mark as they travel the remaining distance to the substrate with little further development. The aggregate particle sizes tend to evolve rather smoothly. The curves are characterized by a slower growth rate in the early stage between 3.85cm and 3.0cm, but then there is a sharp increase in the slope of the curve as the particles enter the hot zone and continue to aggregate until reaching the substrate.

In these cases, the data suggests strongly that the characteristic coalescence time is long compared to the rate of collisions leading to coagulation. As the flame temperature cools down near the 1.0cm mark, agglomerated particles will cease to coalesce fully. Primary particle sizes will essentially be frozen (as seen by the plateau in [Figure 5.3](#)) and the

aggregate particle sizes will continue to grow and include more partially-sintered primary particles.

5.3 Sectional model simulations of the standard cases

Sectional models with a geometric spacing factor of $q=1.2$, which corresponds to 102 volume sections, are run for each of the three standard cases. Computational time for these simulations is usually around thirty-six (36) hours using an Intel® Pentium® 2.80 GHz CPU. The geometric standard deviation (GSD) for all three cases settles on 1.462 by the time the particles arrive at the substrate. This is in good agreement with values reported by Vermury *et al.*²⁰ and Talukdar *et al.*²¹ The GSD with respect to particle residence time is shown in Figure 5.5.

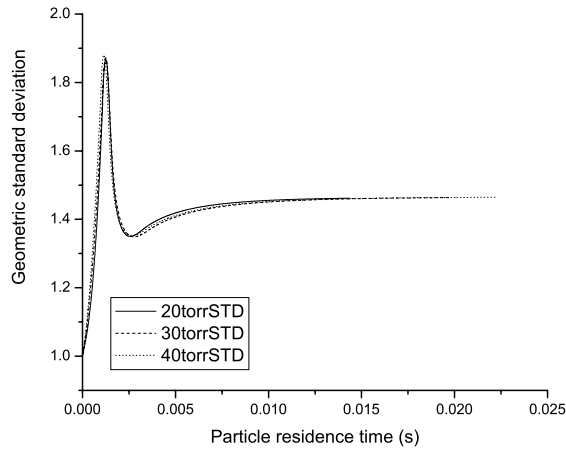


Figure 5.5. Geometric standard deviation with respect to particle residence time for the standard cases as calculated by the sectional model.

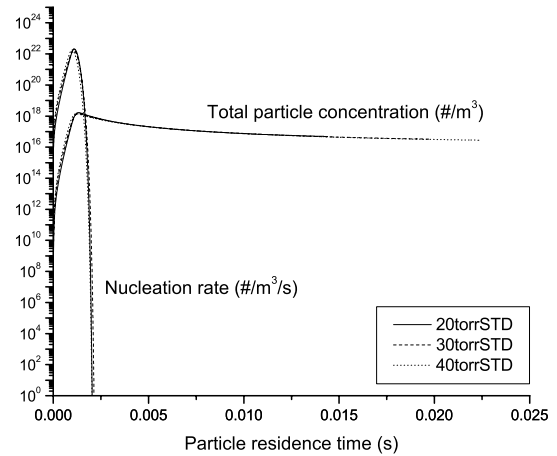


Figure 5.6. Particle concentration and nucleation rate with respect to particle residence time for the standard cases as generated by the sectional model.

The nucleation rate for all three cases peaks at around 1.1ms. This is slightly before the maximum total particle concentration, which is seen for all three cases to be around 1.32ms. As the precursor vapor homogeneously nucleates into monomers, some time

will elapse before the critical cluster size is achieved, and nano-TiO₂ particles can be accounted for. Up until this time, nucleation dominates. After the peak at 1.32ms, the total particle concentration decreases slightly and plateaus. During this time, particle-to-particle coagulation, coalescence, and surface growth are active in generating larger primary particles and larger aggregates. The nucleation rate and total particle concentration as a function of particle residence time is given in [Figure 5.6](#).

[Figure 5.7](#) and [Figure 5.8](#) display calculated primary and aggregate particle sizes from the sectional model. For the 20torrSTD case, the primary particle size at the substrate is 5.12nm, and the aggregate particle size is 21.90nm. For the 30torrSTD case, primary particle sizes at the substrate are found to be 4.03nm, and the aggregate particle sizes are 24.98nm. For the 40torrSTD case, primary particles sizes are calculated to be 3.57nm, and aggregate particle sizes are 26.25nm.

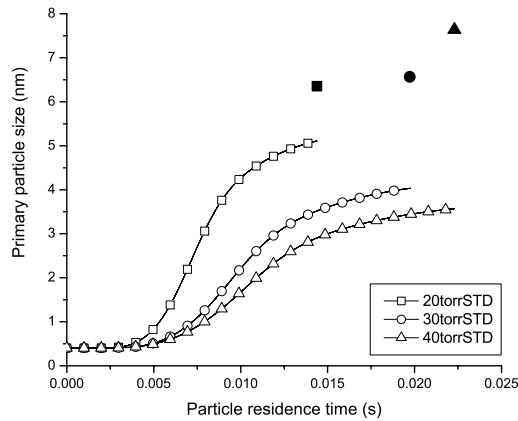


Figure 5.7. Primary particle sizes with respect to particle residence time for the standard cases as calculated by the sectional model. Shape-corresponding data points have been added to mark experimental results by BET measurement.

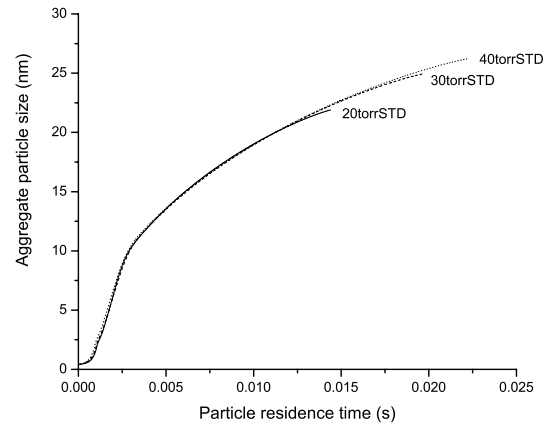


Figure 5.8. Aggregate particle sizes with respect to particle residence time for the standard cases as calculated by the sectional model.

These three standard cases show a decreasing trend in primary particle sizes but an increase in aggregate particle sizes for cases as pressure increases from 20 to 40torr. As expected, the aggregate particle sizes increase with longer particle residence times. The longer the particles experience a high temperature in the flame, the more coalescence proceeds with ease, and the particles continue sintering until they are joined completely into one new larger spherical particle; however, coagulation time is shorter than that of coalescence in our moderate temperature flame. Primary particles show a decrease in size as their growth is suppressed as larger aggregates take longer to coalesce than to coagulate, with the primary particle size leveling off before reaching the substrate.

5.4 Ex-situ nanoparticle characterization from the substrate

The nanopowders generated by the three standard cases have all been characterized using the methods described earlier in Chapter 3. The water-cooled substrate is used to quench the particles and inhibit further growth. The characterized sample is collected only from the area on the substrate where the cover plate is located during the initial transient stage of the flame. Details of this process have been given in Chapter 3. The powder samples are analyzed using the XRD and BET methods to determine particle phase and crystallinity, specific surface area, and primary particle size.

5.4.1 XRD

The synthesized powders in this work show the presence of the Anatase and rutile phases of titania. MDI Jade software is used for qualitative analysis of the collected spectra. However, pattern refinement via a whole-pattern fitting (Rietveld) method encounters difficulties due to the amorphous humps and slight shifts in peak position. A

characteristic pattern of the powders synthesis is given in Figure 5.9. Anatase peaks are visible at (101), (103)/(004)/(112), (200), (105)/(211) and (204) according to powder diffraction file (PDF) #97-020-0392.

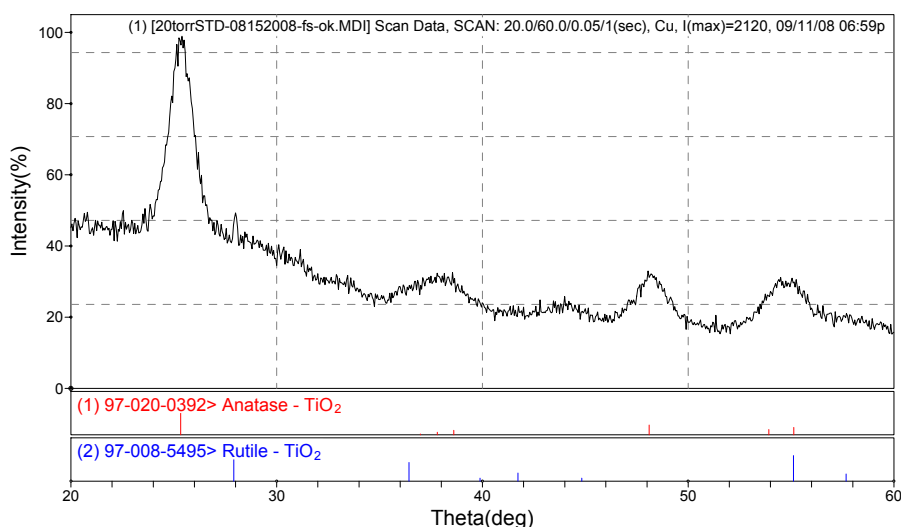


Figure 5.9. Characteristic XRD pattern for the powders synthesized under the standard flame synthesis conditions. Present phases are anatase and rutile titania.

Qualitative analysis indicates that the powder samples generated in the flame synthesis configuration used in this work are >85% anatase titania, where the rest of the composition is made up of the rutile phase.

5.4.2 BET

The specific surface area (SSA) of the synthesized particles is determined by gas-adsorption with nitrogen using the BET method. For the 20torrSTD case, the specific surface area is found to be 245.873m²/g. Assuming spherical particles, this SSA corresponds to a primary particle size of 6.36nm. The 30torrSTD case shows a SSA of

237.872m²/g which corresponds to a primary particle size of 6.57nm. The 40torrSTD case gives a SSA of 204.616m²/g corresponding to a primary particle size of 7.64nm.

These trends show decreasing SSA and increasing primary particle sizes as the ambient pressure increases from 20 to 40torr. These trends are the opposite of those generated by the sectional model. However, primary particle sizes, as determined by transmission electron microscopy (TEM) images, are 5.97nm, 5.88nm, and 5.45nm for the same 20, 30, and 40torr parameters, respectively.²² Thus, the apparent discrepancy may be due to the BET accounting for reduction of surface area for particles that have undergone partial sintering with necking between them, giving smaller SSA and higher extracted values for primary particle sizes. It is suggested here that particles synthesized in the 40torrSTD case experience greater effects of partial sintering but incomplete coalescence due to their longer residence times.

5.5 Conclusions

Three sets of standard synthesis conditions have been established and have been used to validate the accuracy and ability of the numerical models to predict particle growth trends. Primary particle sizes, as determined by the monodisperse model, are low but show the same trends as those calculated by the sectional model. Aggregate particle sizes from the monodisperse model are significantly larger than those from the sectional model, but the trends remain the same. The monodisperse model used here appears to be suitable for determining trends in primary and aggregate particle size growth, but the limitations of the model and its assumptions make it impractical for accurate predictions of final primary and aggregate particle sizes.

The sectional model consistently under-predicted the final primary particle sizes as compared with experimental results characterized using the BET method. These discrepancies are attributed to partial sintering of primary particles into aggregates causing necking between particles to occur. This partial sintering results in reduced specific surface areas leading to the extraction of larger primary particle sizes.

Chapter 6

Ambient Pressure Effect on Flame Synthesis of TiO₂ Nanoparticles

In the previous chapter, three standard cases were defined in order to provide a baseline for comparison. In this chapter, the 20torr standard case is compared to modified 30torr and 40torr cases which have matching temperature profiles and gas-phase velocity profiles over the 4cm substrate-burner gap. Experimental results are characterized and compared to the monodisperse and sectional model predictions.

6.1 Background and objectives

Low-pressure environments are known to be advantageous in combustion synthesis of nanomaterials. Under low-pressure, inter-particle collisions, which lead to coagulation, are reduced, reducing particle agglomeration. Besides low-pressure environments, time/temperature histories experienced by synthesized particles play a major role in particle growth and evolution. Flame parameters such as fuel and oxidizer, stoichiometric ratio, flow rate, diluent, substrate-burner gap distance, and cooled substrate temperature can all be used to fix time/temperature histories for synthesized particles.¹² In this work, adjustments to flow rate and diluents (type and quantity) have been used in order to isolate ambient pressure and observe its effect on particle growth and evolution.

The standard cases presented in Chapter 5 have differing gas-phase inlet velocities at the burner plate and consequently the particle residence times are not identical. As compared

to the standard 30 and 40torr cases, modified 30 and 40torr cases are used where helium gas is substituted for a portion of the nitrogen diluent. Helium is selected because it is inert and much lighter than the diatomic nitrogen used in the standard cases. After setting the inlet gas-velocities of the modified 30 and 40torr cases to 150cm/s, the helium swap with the nitrogen makes it possible to match the temperature history of the flames in addition to the gas-phase velocity profiles of the flow fields. In doing this, the temperature and residence time effects are eliminated and the pressure effect is isolated.

6.2 Experiment

The 20torrSTD case remains unchanged from Chapter 5. The modified 30torr case used in this pressure study (30torrHE) has $\text{H}_2/\text{O}_2/\text{N}_2/\text{He}$ ratios of 1.0:1.213:1.1240:0.5879 and a mass flux of 3.432mg/s/cm^2 . The modified 40torr case used in this chapter (40torrHE) has $\text{H}_2/\text{O}_2/\text{N}_2/\text{He}$ ratios of 1.0:1.213:1.4023:1.2011 and a mass flux of 4.241mg/s/cm^2 . All three cases have a precursor-loading rate of 6.45×10^{-4} mol/min. Tabulated parameters for these three cases are shown in [Table 6.1](#). All cases have an equivalence ratio of 0.42 so that the flames remain lean. It is noted that the excess oxygen afforded by the lean flame is advantageous in synthesizing oxide nanopowders.

H_2/O_2 ($\phi=0.42$)	H_2	O_2	N_2	He	Inlet gas velocity (cm/s)	Mass flux (mg/s/cm^2)	Precursor-loading rate (mol/min)
20torrSTD	1.0	1.213	0.7377	---	150	2.519	6.45 E-4
30torrHE	1.0	1.213	1.1240	0.5879	150	3.432	6.45 E-4
40torrHE	1.0	1.213	1.4023	1.2011	150	4.241	6.45 E-4

Table 6.1. Experimental parameters for the pressure study cases.

The Sandia SPIN code is again used for the modified 30 and 40torr cases. With the removal of the diatomic nitrogen, the heat capacity of the flame is decreased, and the temperature profiles rise dramatically over that of the 20torrSTD case. To alleviate the high temperatures and to bring the velocity profiles more inline with each other, a light inert helium gas is added.

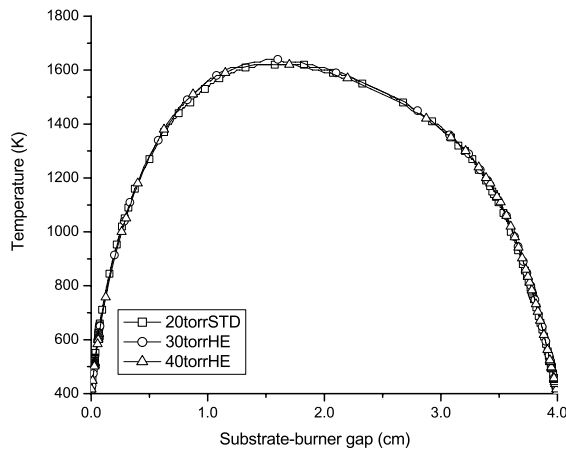


Figure 6.1. Temperature profiles with respect to gap distance for the pressure cases as generated by the modified Sandia SPIN code.

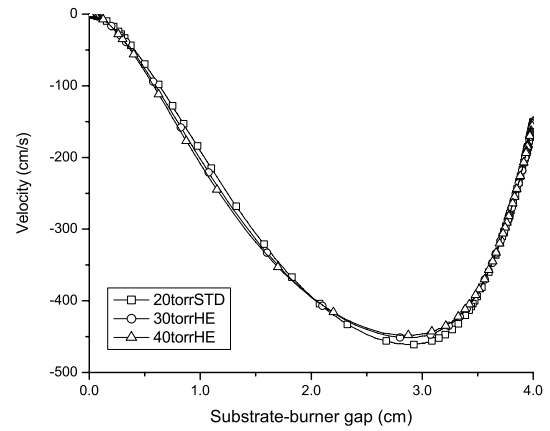


Figure 6.2. Gas-phase velocity profiles with respect to gap distance for the pressure cases as generated by the modified Sandia SPIN code.

In the modified 30 and 40torr cases, the cold-gas velocity at the burner exit is increased to 150cm/s to match that of the 20torrSTD case. By the substitution of helium for nitrogen diluent used in the 30 and 40torrSTD cases, the temperature histories are matched as well as the velocity profiles. These profiles are seen above in [Figure 6.1](#) and [Figure 6.2](#). This means that the particles in the flame now see the same temperature at every x-position between the burner and the substrate. Furthermore, since the velocity profiles are matching, the residence times are the same and it can be said that the particles

are experiencing the same temperature history in each flame case presented in this chapter.

6.3 Results and discussion

In the next two sub-sections, the monodisperse model and sectional model results are presented and discussed. Following, there is a sub-section where the *ex-situ* particle characterization results are presented and compared to the particle growth models.

6.3.1 Monodisperse model results

The monodisperse model is again employed to simulate the growth and evolution of the primary and aggregate particle sizes for these cases involving identical temperature and velocity profiles (i.e. residence times). The flow field databases generated by the SPIN code are used as input again for this growth model. The same incorporation of a shape factor is again employed with the same form as indicated in Eq. (4.3), where the α/β values are 8.5/6.0. The predicted primary and aggregate particle sizes versus position are presented below in [Figure 6.3](#) and [Figure 6.4](#). The temperature history as seen by the monodisperse model is given in [Figure 6.5](#).

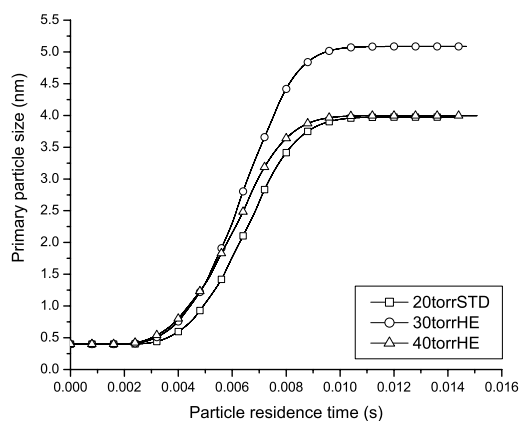


Figure 6.3. Primary particle size with respect to gap distance as calculated by the monodisperse model for the pressure cases.

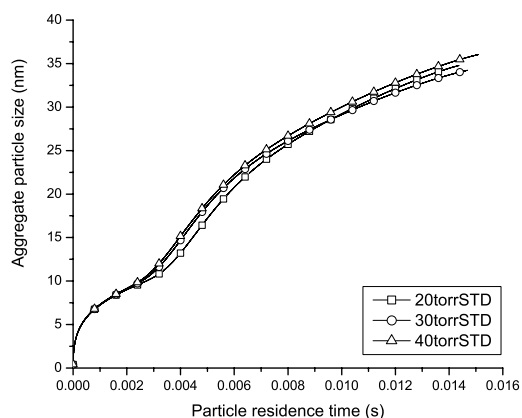


Figure 6.4. Aggregate particle size with respect to gap distance as calculated by the monodisperse model for the pressure cases.

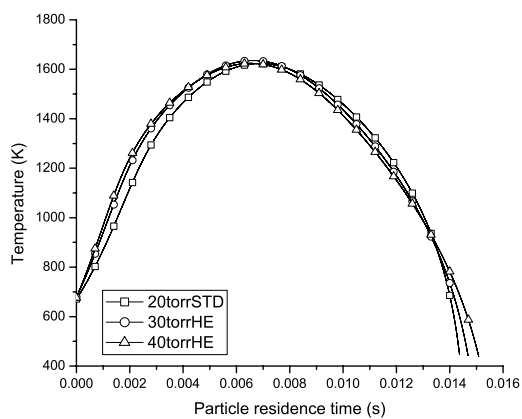


Figure 6.5. Temperature history with respect to particle residence time as seen by the monodisperse model for the pressure cases.

In a fashion similar to the results presented for the standard cases in Chapter 5, the primary particles again show slow development initially but then a sharp increase as they travel through the hot flow field. The aggregates again show an increase in their growth rate near the 3.0cm mark as they enter the hot zone of the flame structure. Note the non-monotonic size for increasing pressure. The final 30torr primary particle size is larger than that for 40torr, which is larger than that for 20torr. The aggregate particle sizes are the same for all cases, which is reasonable since the temperature histories are identical. Thus, the trend in primary particle size is likely due to the effect of pressure on the relative rates of coagulation and coalescence.

6.3.2 Sectional model results

As in the previous chapter, sectional models with a geometric spacing factor of $q=1.2$ corresponding to 102 volume sections are employed to model the 30 and 40torrHE cases. Results for the 20torrSTD case remain unchanged. Computational time for these cases is also around thirty-six (36) hours with a Intel® Pentium® 2.80GHz processor. The geometric standard deviation (GSD) of these cases remains 1.462 when the particles are at the substrate. The GSD is shown as a function of particle residence time in [Figure 6.6](#). As nucleation and coagulation fight to be the dominant growth mechanism early on during synthesis, the GSD rises sharply to a local maximum of 1.867 until coagulation takes over and leads to coalescence. The modified 30 and 40torr cases using helium show an earlier rise to the maximum GSD and also an earlier arrival to the final value of 1.462 at the substrate.

A plot of the nucleation rate and the total particle concentration with respect to particle residence time is given in Figure 6.7. It is observed that the modified 30 and 40torr cases involving helium reach the local maximums for nucleation rate and total particle concentration sooner than the 20torrSTD case. This is expected as the total dilution of the 30 and 40torrHE cases is reduced (notably a 50% reduction in the presence of the nitrogen diluent) from the standard cases presented in Chapter 5. This reduction in dilution and the removal of heavy nitrogen molecules from the combustion gases drive particle nucleation to the forefront early on during synthesis. Once the monomer clusters reach the critical size, they are considered TiO_2 nanoparticles and undergo stronger effects from coagulation, coalescence, and surface growth.

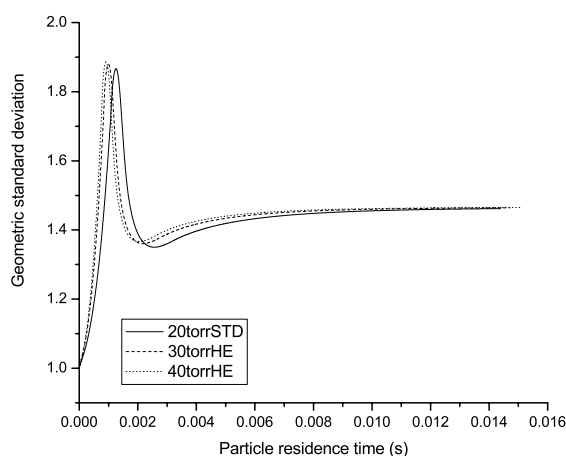


Figure 6.6. Geometric standard deviation with respect to particle residence time as calculated by the sectional model for the pressure cases.

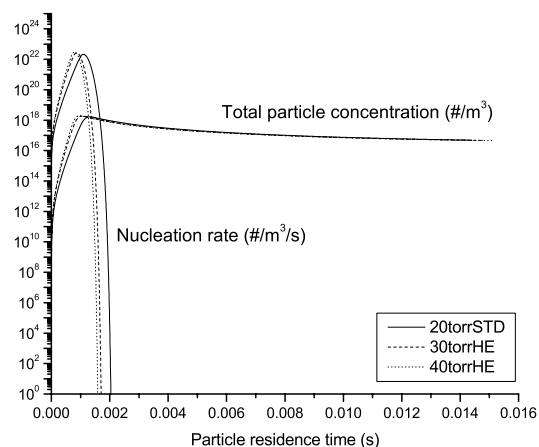


Figure 6.7. Total particle concentration and nucleation rate with respect to particle residence time as calculated by the sectional model for the pressure cases.

The primary particle sizes and aggregate particle sizes calculated by the sectional model can be shown in Figure 6.8 and Figure 6.9. The 20torrSTD results are the same as from the previous chapter. The primary particle size for the 30torrHE case is 6.16nm, and the

aggregate size is 22.22nm. For the 40torrHE case, the primary particle size reaches a final value of 5.72nm and a final aggregate particle size of 22.44nm. It is noted here that the primary particle sizes for all three cases are within roughly 1nm of each other.

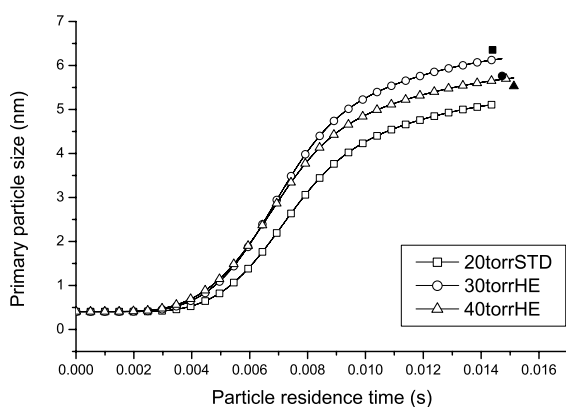


Figure 6.8. Primary particle size with respect to residence time as calculated by the sectional model.

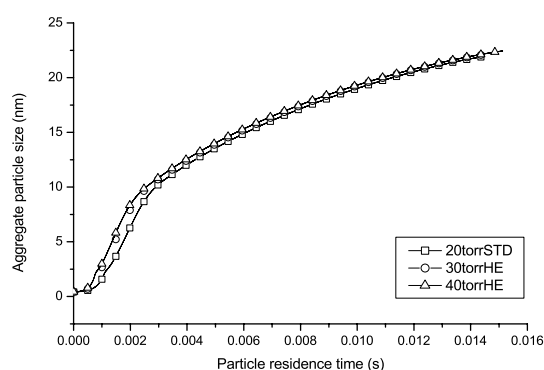


Figure 6.9. Aggregate particle size with respect to residence time as calculated by the sectional model.

In Chapter 5, it was observed that aggregate particle sizes increase with increasing residence time. This conclusion is validated in this chapter as the residence times are very closely matched among these cases, and the aggregate particle sizes show little difference. A slight increase is seen as the ambient pressure increases, but this effect is obviously very small in comparison to the effect of particle residence time on aggregate particle sizes. Primary particle sizes show no clear trend based solely on pressure increase. There is a size jump up between the 20 and 30torr cases here but then a drop back down between the 30 and 40torrHE cases. The decrease in dilution is again noted in the 30 and 40torrHE cases and is expected to be the reason for coalescence taking a secondary role to coagulation, where particles share only a point of contact on their surface and may continue to develop as larger primary particles due to surface growth.

6.3.3 Ex-situ powder characterization

Again with these cases, the powder samples have been characterized *ex-situ* using the various methods described earlier in Chapter 3. Powder samples are collected only from the clean substrate after the flame has stabilized and the cover plate has been removed. The samples are characterized using the XRD and BET methods to determine particle phase crystallinity, specific surface area, and primary particle size.

6.3.3.1 XRD

XRD results indicate anatase as the dominant phase. The composition of the powders is >90% anatase and the remainder is rutile. [Figure 6.10](#) and [Figure 6.11](#) show the collected spectra.

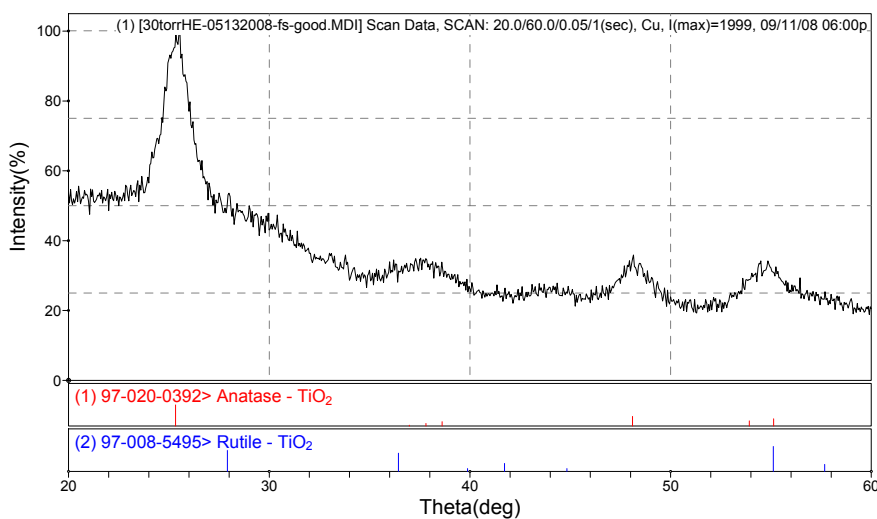


Figure 6.10. XRD pattern for 30torrHE case.

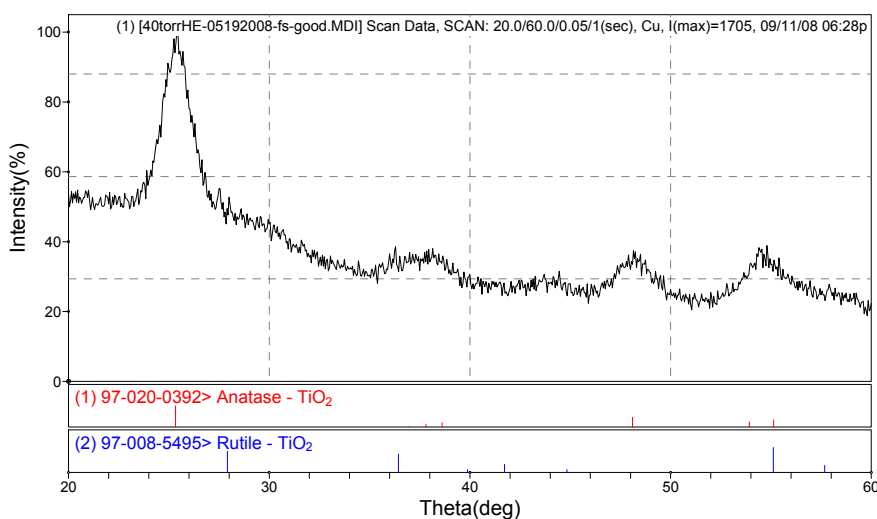


Figure 6.11. XRD pattern for 40torrHE case.

6.3.3.2 BET

The BET method using gas-adsorption with nitrogen at liquid nitrogen temperatures is used to determine specific surface area (SSA). Assuming spherical particles, the primary particle sizes are calculated from the SSA. As reported in Chapter 5, the SSA for the 20torrSTD case is $345.87\text{m}^2/\text{g}$ which gives a primary particle size of 6.36nm. For the 30torrHE case, the SSA is $271.10\text{m}^2/\text{g}$ which gives a primary particle size of 5.76nm. Finally, the 40torrHE case shows a SSA of $282.55\text{m}^2/\text{g}$ corresponding to a primary particle size of 5.53nm.

The substitution of light helium gas in place of the heavier nitrogen diluent in the 30 and 40torr cases causes a decreasing trend in primary particle sizes for increasing ambient pressures. However, the absolute difference between the three cases is only $\sim 0.6\text{nm}$. Corresponding to a decreasing primary particle size, the SSA shows an increasing trend

as ambient pressure increases. This suggests that coagulation plays a stronger role than coalescence as ambient pressures increase while time/temperature histories are held constant between cases.

6.4 Conclusions

The effect of ambient pressure is examined experimentally and computationally for flames with identical temperature and gas-phase velocity profiles. This corresponds to identical time/temperature histories for the 20torr and modified 30 and 40torr cases. Ambient pressure is isolated as the variable process parameter.

With matching time/temperature histories and primary particle sizes all differing computationally by $<1\text{nm}$ and experimentally by $<0.6\text{nm}$, it is concluded that the ambient pressure plays a negligible role in primary particle size determination. Aggregate particle sizes are virtually unaffected by ambient pressure changes once the more dominant time/temperature history effects are made a non-factor via strategic dilution with helium. Finally, the increasing trend in specific surface area with increasing ambient pressure suggests that the coalescence growth mechanism plays a smaller role as ambient pressures increase.

Chapter 7

Temperature Effect on Flame Synthesis of TiO_2 Nanoparticles

In the previous chapter, the effect of ambient pressure was studied. In this chapter, the temperature effect is studied both experimentally and computationally. The pressure is maintained at a constant 30torr for all of these cases, and combinations of inert helium and argon are added or completely substituted for nitrogen diluent present in the standard 30torr case presented in Chapter 5.

7.1 Background and objectives

For this temperature effect study, the 30torrSTD case remains unchanged. A modified 30torr case (30torrTRY29) is used, in which all nitrogen dilution from the 30torrSTD case is replaced with a 50/50 split of helium and argon. This ensures that the total dilution of the flame remains unchanged. Another 30torr case (30torrTRY38) is used, in which the nitrogen diluent is substantially reduced and replaced by a combination of helium and argon. In this case, the total dilution of the flame is slightly more than that of the original 30torrSTD case. For both of these cases (30torrTRY29 and 30torrTRY38), strategic dilution again allows for the matching of the gas-phase velocity profiles for all the synthesis flames. For the 30torrTRY29 case, the $\text{H}_2/\text{O}_2/\text{N}_2/\text{He}/\text{Ar}$ ratios are 1.0:1.213:0.0:1.0214:1.0214 with a mass flux of 3.064mg/s/cm^2). The 30torrTRY38 case has $\text{H}_2/\text{O}_2/\text{N}_2/\text{He}/\text{Ar}$ ratios of 1.0:1.213:0.250:1.2214:0.9214 and a mass flux of 3.064mg/s/cm^2).

For the regular 30torrTRY29 and 30torrTRY38 cases, the SPIN code is used to compute the flow field structure (e.g. species, temperature, velocity) which is utilized by the monodisperse model and sectional model for particle growth and evolution. Comparisons of the simulation results are again compared to *ex-situ* characterizations via XRD and BET for particle phase and crystallinity, and specific surface area and primary particle size, respectively.

To assess the role of the inert gas composition, a simple program is written to interpolate and interchange the temperature history information in the flow field databases between the 30torrSTD and the 30torrTRY29 and 30torrTRY38 cases. Sectional models are run for these cases, but experimental results are not available used for comparison, as the exchanged temperature profiles are not technically realistic.

7.2 Experiment

All flames investigated in this chapter have an equivalence ratio of 0.42. The excess oxygen present in lean flames is favorable when synthesizing oxide particles such as nano-titania. Initially, when the diatomic diluent is removed from the 30torrSTD case, the temperature profile rises dramatically. The addition of high-molecular-weight monatomic argon and low-molecular-weight monatomic helium make it possible to match the gas-phase velocity profiles. This helps to make the particle residence times in the flame similar, but, of course, not identical due to viscous drag, particle size, et cetera. The addition of the inert gases also affects the temperature histories. In the case of 30torrTRY38, the temperature profile is made cooler everywhere between the burner and the substrate. The difference in maximum temperatures achieved, as compared to the

standard case, is 80K and shifted roughly 0.25cm towards the burner. For the 30torrTRY29 case, the temperature histories are virtually identical in shape and, with replacement of the inert gases for the nitrogen diluent, the difference in maximum achieved temperature is only 6K and is shifted only 0.25cm closer to the burner. The flame parameters are shown in [Table 7.1](#).

H ₂ /O ₂ ($\phi=0.42$)	H ₂	O ₂	N ₂	He	Ar	Inlet gas velocity (cm/s)	Mass flux (mg/s/cm ²)	Precursor-loading rate (mol/min)
30torrSTD	1.0	1.213	2.0428	--	--	110	3.064	4.73 E-4
30torrTRY29	1.0	1.213	--	1.0214	1.0214	110	3.064	4.73 E-4
30torrTRY38	1.0	1.213	0.2500	1.2214	0.9214	110	3.064	4.73 E-4

Table 7.1. Experimental parameters for the temperature study cases.

The temperature histories for the new 30torrTRY29 and 30torrTRY38 cases, in addition to the gas-phase velocity profiles, are given in [Figure 7.1](#) and [Figure 7.2](#), respectively. Using the inert gases and the same initial gas-phase velocity at the burner (110cm/s), the velocity profiles are similar for each of the flow fields, which help to moderate particle residence time as a factor affecting the growth of the nanoparticles. Achieving a hotter temperature profile using such inert gas swapping was not feasible, so a similar temperature profile and a colder temperature profile are used. In the case of the matching temperature profiles, it is investigated whether the strategic dilution with inert gases in place of nitrogen plays a significant role in the particle growth as determined by the monodisperse and sectional models.

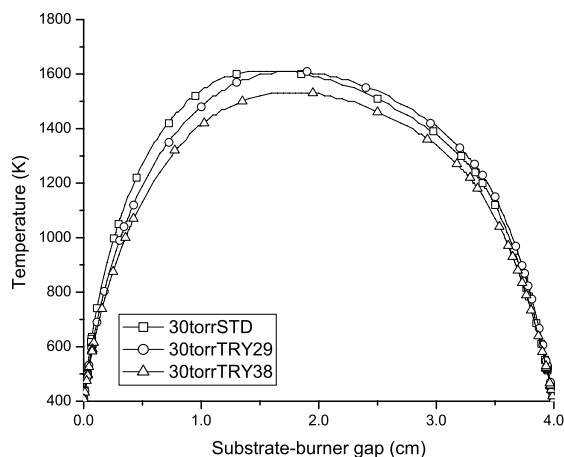


Figure 7.1. Temperature with respect to gap distance for the temperature study cases.

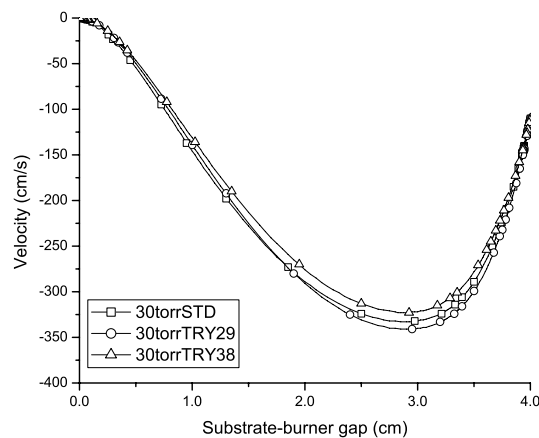


Figure 7.2. Velocity with respect to gap distance for the temperature study cases.

7.3 Results and discussion

In the following sub-sections, the monodisperse model and sectional model results are presented and discussed. Results from *ex-situ* powder characterization are presented and compared with the computational models. Following these discussions, a purely computational investigation into the temperature effect and the role of diluents in particle growth is presented.

7.3.1 Computational models verified with experimental results

A similar approach to that found in Chapter 6 is again used to compare the monodisperse model and sectional model results to those obtained by *ex-situ* particle characterization.

7.3.1.1 Monodisperse model results

The same monodisperse model is again employed to simulate the growth and evolution of the primary and aggregate particle sizes for these cases involving a similar temperature profile with helium and argon substitution for nitrogen and a colder temperature profile

incorporating all three diluent gases. In all cases, the velocity profiles are identical so as to help eliminate particle residence time and its effects on particle development in the flame. Flow field databases from the SPIN code are used in a fashion similar to Chapters 5 and 6. The shape factor takes the same form here and the α/β values are again kept constant at 8.5/6.0. Primary particle and aggregate particle sizes with respect to particle residence time are given in Figure 7.3 and Figure 7.4. The temperature history as seen by the monodisperse model is seen in Figure 7.5.

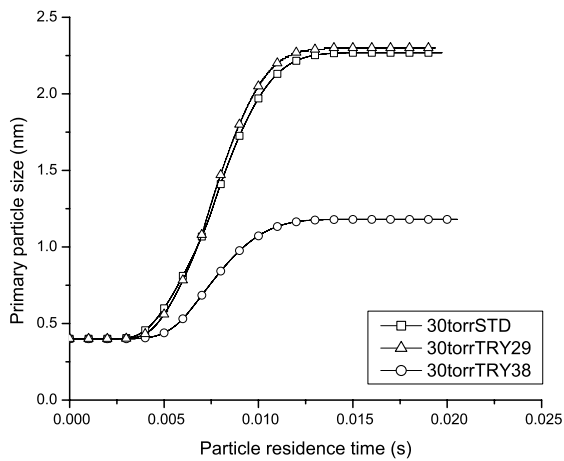


Figure 7.3. Primary particle size with respect to particle residence time as calculated by the monodisperse model.

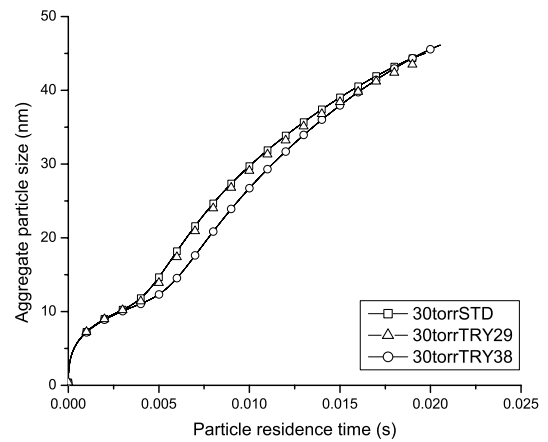


Figure 7.4. Aggregate particle size with respect to particle residence time as calculated by the monodisperse model.

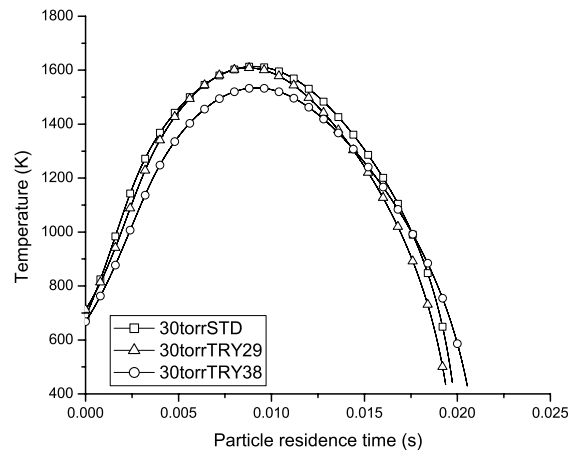


Figure 7.5. Temperature history used in monodisperse model calculation for temperature study cases.

Similar curve shapes to those seen in Chapters 5 and 6 are again noted here. A brief period of slow development in primary particle size is followed by a steep rise as the particles travel through the hot flow field. And again, as the characteristic coalescence time becomes long as compared to the rate of collisions leading to aggregation, primary particles freeze in size and plateau as they arrive at the substrate. Aggregate particle sizes evolve smoothly throughout the gap distance. There is, however, a noticeable increase in growth rate as the aggregates enter the hot zone of the flame. The aggregate particles continue to develop steadily as more primary particles become partially sintered within existing aggregates.

7.3.1.2 Sectional model results

Sectional models with a spacing factor of $q=1.2$, corresponding to 102 volume sections, are employed to model the 30torrTRY29 and 30torrTRY38 cases. Results reported in Chapter 5 for the 30torrSTD case are unchanged. These cases again converge to a geometric standard deviation (GSD) of 1.462 for particles reaching the substrate. The GSD as a function of particle residence time is shown in [Figure 7.6](#). A local GSD maximum of 1.847 is reached near the 3.72cm mark. At this time, coagulation overtakes nucleation and surface growth as the dominant growth mechanism.

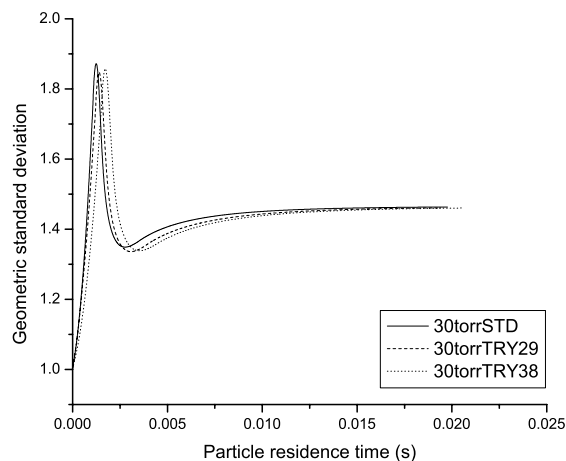


Figure 7.6.: Geometric standard deviation with respect to particle residence time as calculated by the sectional model.

The primary and aggregate particle sizes calculated by the sectional model are given in [Figure 7.7](#) and [Figure 7.8](#). The primary particle size for the 30torrTRY29 case is 3.64nm with aggregate particle sizes of 24.62nm. The 30torrTRY38 case generates a primary particle size of 1.59nm with aggregate particle size of 24.83nm.

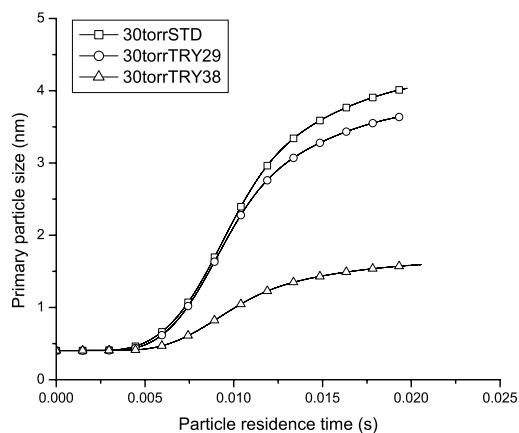


Figure 7.7. Primary particle size with respect to particle residence time as determined by the sectional model.

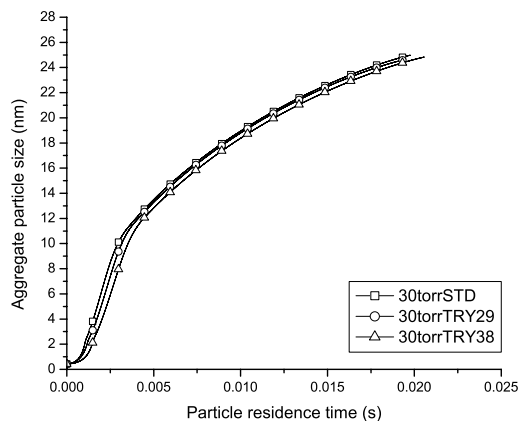


Figure 7.8. Aggregate particle size with respect to particle residence time as determined by the sectional model.

Aggregate particles again show $<0.5\text{nm}$ difference among the three cases presented. This, again, is due to the matched velocity profiles and the correspondingly similar residence times. Primary particle sizes vary by $<0.5\text{nm}$ between the 30torrSTD and 30torrTRY29 cases. As indicated previously, the difference between these two flames are the diluent gases. The temperature histories and velocity profiles are similar, and it is expected that primary particle sizes, as well as the aggregate particle sizes, would be the same. Lower flame temperatures in the 30torrTRY38 case principally affect characteristic coalescence times, as these times should be much longer at low temperatures. There is a $>2\text{nm}$ difference in sizes between the 30torrTRY38 case with reduced temperatures and the 30torrSTD and 30torrTRY29 cases with hotter temperature histories.

7.3.2 Ex-situ powder characterization

Again in this chapter, the powder samples are characterized *ex-situ* using the various methods described earlier in Chapter 3. Powder samples are collected only from the clean substrate after the flame has stabilized and the cover plate has been removed. The samples are characterized using the XRD and BET methods to determine particle phase crystallinity, specific surface area, and primary particle size.

7.3.2.1 XRD

XRD results indicate anatase as the dominant phase. This is readily observable by the relative peak intensities of the strongest phase peaks as shown in [Figure 7.9](#) and [Figure 7.10](#). Profile refinement to quantitatively assess the weight percentages of the two phases encounters difficulty due to the amorphous humps and minor peak shifts. However, the composition of the powders is $>85\%$ anatase and the remainder is rutile.

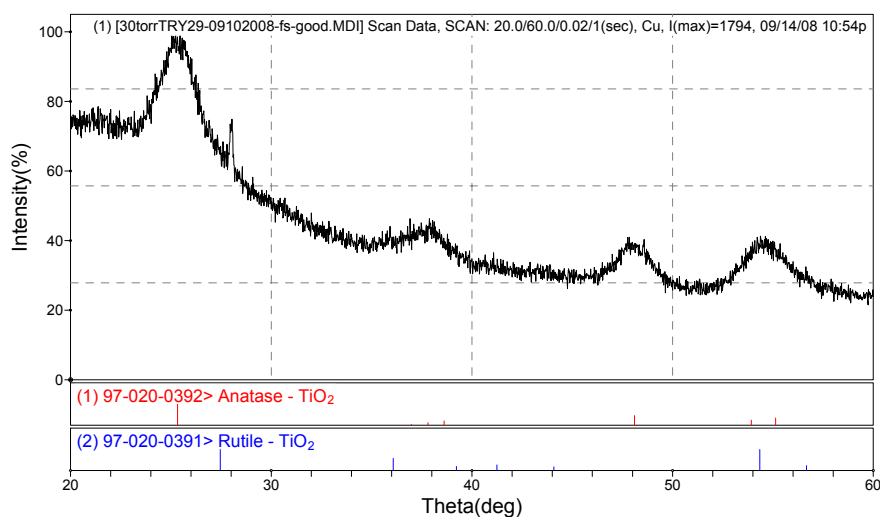


Figure 7.9. XRD pattern for 30torrTRY29 case.

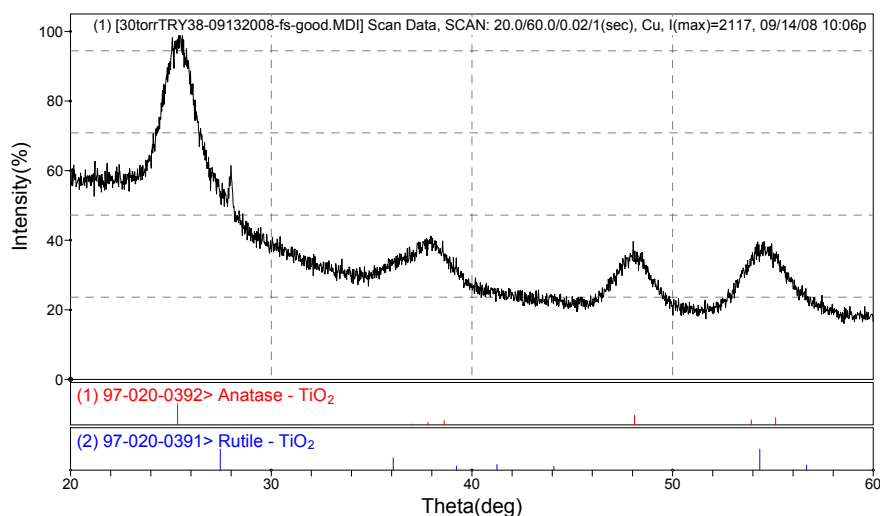


Figure 7.10. XRD pattern for 30torrTRY38 case.

7.3.2.2 BET

The BET method using gas-adsorption with nitrogen at liquid nitrogen temperature is used to determine specific surface area (SSA). Assuming spherical particles, the primary particle sizes are then extracted from the SSA information. As reported in Chapter 5, the SSA for the 30torrSTD case is $237.87\text{m}^2/\text{g}$, and the extracted primary particle size is

6.57nm. For the 30torrTRY29 case, the SSA is calculated to be $262.95\text{m}^2/\text{g}$, which corresponds to a primary particle size of 5.94nm. The 30torrTRY38 case generates a SSA of $328.96\text{m}^2/\text{g}$, with an extracted primary particle size of 4.75nm.

The 30torrSTD and 30torrTRY29 cases reveal a $<0.6\text{nm}$ difference in primary particle sizes. For the same total dilution, the substitution of inert helium and argon for nitrogen makes little difference in the final primary particle size. The 30torrTRY38 case, with reduced temperatures at every point between the burner and the substrate, generates powders with a significantly smaller primary particle size ($\sim 1.2\text{nm}$) which compares well with the predictions of both the monodisperse model and the sectional model.

7.3.3 A Computational Investigation into the Density Effect

Suspecting particle growth can be affected by the use of inert diluent composition (e.g. use of argon instead of nitrogen), a simple MATLAB program is used to interpolate temperature profile points of differing grid sizes. These interpolated temperature profiles are exchanged between the 30torrSTD case and the 30torrTRY29 and 30torrTRY38 cases. [Figure 7.1](#) shows the profiles that have been exchanged. Sectional models with a geometric spacing factor of $q=1.2$ are again used to predict particle growth and evolution. Primary particle and aggregate particle sizes for both cases of interchanged temperature histories are presented in [Figure 7.11](#) through [Figure 7.14](#).

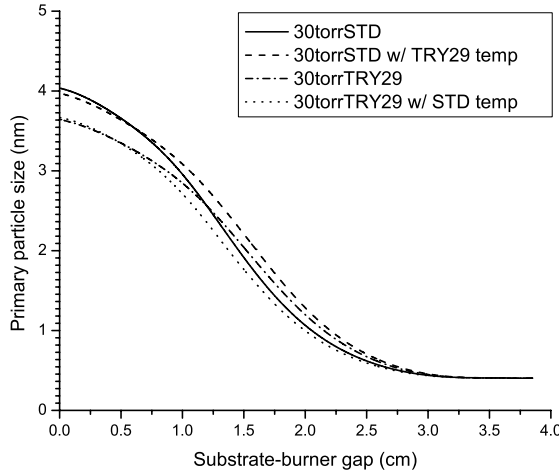


Figure 7.11. Primary particle size with respect to gap distance for the 30torrSTD case, 30torrTRY29 case, and both of those cases with the exchanged temperature profiles.

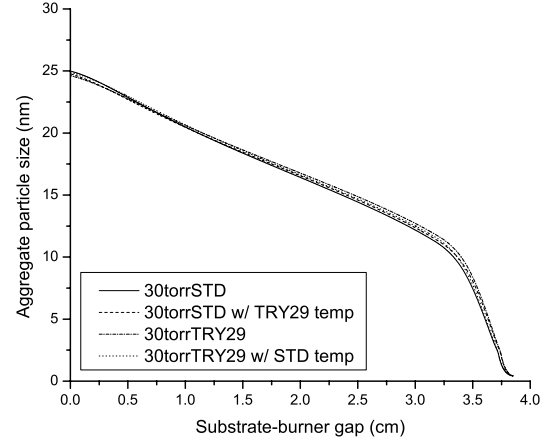


Figure 7.12. Aggregate particle size with respect to gap distance for the 30torrSTD case, 30torrTRY29 case, and both of those cases with the exchanged temperature profiles.

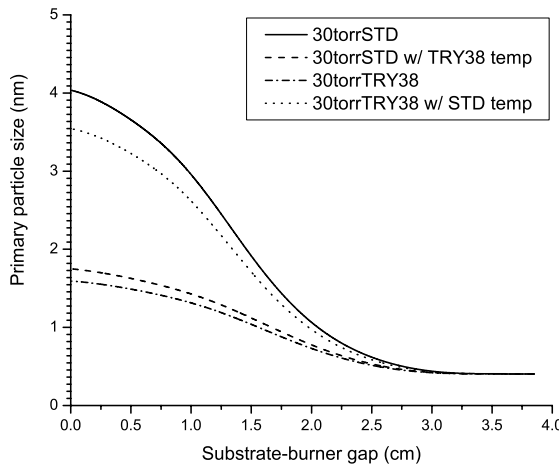


Figure 7.13. Primary particle size with respect to gap distance for the 30torrSTD case, 30torrTRY38 case, and both of those cases with the exchanged temperature profiles.

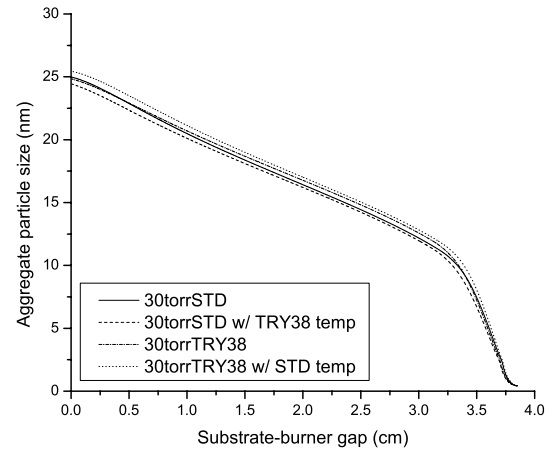


Figure 7.14. Aggregate particle size with respect to gap distance for the 30torrSTD case, 30torrTRY38 case, and both of those cases with the exchanged temperature profiles.

After exchanging temperature profiles between the 30torrSTD case and the 30torrTRY29 case, there is no noticeable change in aggregate particle sizes. This is expected as the temperature profile swap has no effect on the residence time of the particles in the flame, which is already determined to be the dominant factor controlling aggregate particle size. Final primary particle size shows negligible difference between the original 30torrTRY29

and the one using the 30torrSTD temperature profile. This is the same for the original 30torrSTD and the one using the exchanged temperature profile. Differences $<0.5\text{nm}$ are observed between the 30torrSTD and 30torrTRY29 primary particle sizes. These slight differences are attributed to the density effect created by the use of different (helium and argon) diluents in place of nitrogen. The slight shift of the standard temperature profile and the 30torrTRY29 temperature profile are likely only responsible for determining the path the particles travel, but not the final primary particle size.

As expected, the exchange of the temperature profiles between the 30torrSTD case and the 30torrTRY38 case again appears to play a negligible role as compared to particle residence time in the evolution of aggregate particles. However, temperature appears to play a very significant role in primary particle development. Primary particle sizes are strongly dependent on the temperature profile found in the flow field database inputted into the sectional model. Final primary particle sizes for the 30torrSTD case and the 30torrTRY38 case using the standard temperature profile are only about 0.5nm apart. Similarly, final primary particle sizes between the 30torrTRY38 case and the 30torrSTD case using the colder temperature history are $<0.2\text{nm}$ apart. Thus, it is determined that the primary particle development is very strongly correlated to the temperature history experienced in the flame and partially affected by the density of the inert gas combination used in dilution. The slight differences (0.5nm and 0.2nm) are again attributed to the use of the inert gas diluents used in addition to, or in complete substitution of, nitrogen diluent.

7.4 Conclusions

The effect of temperature on particle development is experimentally and computationally examined. The ambient pressure is maintained at 30torr, and inert diluents are added and/or substituted for the original nitrogen diluent so as to isolate the temperature effect. Particles synthesized in the 30torrTRY38 case with a colder temperature history exhibit smaller primary particle sizes (differences of $>2\text{nm}$) as compared to the standard 30torr case. *Ex-situ* BET measurements verify these results as the primary particle size of the 30torrTRY38 case is experimentally $\sim 1.2\text{nm}$ smaller than the primary particles generated by the other cases with hotter temperature histories. A computational investigation into the specific role of the temperature history, as inputted into the growth models from the flame structure simulation, indicates that the temperature history significantly affects the primary particle size, but not the aggregate particle size. The use of different diluent gases also generates density effects observable in primary particle size. However, these effects are secondary to the effect of the temperature on the primary particle development.

Chapter 8

Concluding Remarks

Premixed $\text{H}_2/\text{O}_2/\text{inert(s)}$ flat flames in low-pressure environments are seeded with metal-organic TTIP precursor, and used to produce TiO_2 nanopowders. A modified Sandia SPIN code is used to compute the flame structure of this quasi one-dimensional flame geometry. A monodisperse model, accounting for particle coagulation and coalescence, and a sectional model, accounting for particle coagulation, coalescence, and surface growth, are employed to predict primary and aggregate particle sizes. These simulation results are compared with experimental results, as characterized *ex-situ* by XRD and BET measurements. The work presented here aids in understanding the fundamental growth mechanisms behind nanoparticle formation and development, leading to the possibility of using flame synthesis to produce tailored nanoparticles at high rates.

8.1 Review of results and conclusions

Many factors related to the combustion process influence final nanoparticle characteristics. In this work, pressure and temperature are specifically addressed. Gas-phase synthesis methods (i.e. flame synthesis) are a promising means to nanoparticle production given their scalability but are far from fully understood. A summary of the results and conclusions drawn from this work are presented below.

8.1.1 Effects of pressure on particle growth

The effect of ambient pressure on particle characteristics is investigated. The addition of inert helium as diluent (in conjunction with nitrogen) facilitates the simultaneous matching of temperature profiles and gas-phase velocity profiles for cases examined at different pressures (i.e. 20, 30, and 40torr). As such, the temperature histories are the same, ensuring uniformity of final aggregate particle sizes and maintaining nearly constant final primary particle sizes. Differences of <1nm in primary particle size are found both computationally and experimentally, likely due to the effect of gas molecule concentration.

8.1.2 Effects of temperature on particle growth

The effect of temperature on particle characteristics is experimentally and computationally examined. With ambient pressures maintained at 30torr, strategic dilution with inert helium and argon (with or without the use of nitrogen) facilitate the probing of the temperature effect on particle growth, with identical gas-phase velocities for all cases. The cooler temperature history results in the creation of much smaller primary particles. This is due to the substantially longer characteristic coalescence times found at lower temperatures, where primary particle size development is essentially frozen. Identical gas-phase velocity profiles ensure similar particle residence times in the flame and, thus, similar final aggregate particle sizes.

8.2 Suggestions for future work

The experimental setup used in this work is already prepared for the addition of a second precursor in order to produce multi-component nanomaterials. Specifically, silver doping,

using precursors such as silver lactate, can be investigated. Similar processes for particle creation from gas-phase precursors are found for multi-component material synthesis as those which are observed in single-component synthesis, specifically, chemical reactions leading to nucleation and to particle growth. Of interest in doping with silver is the final crystallinity of the silver-doped TiO_2 powders. The silver could create a coating around the TiO_2 particles, be arranged orderly, or be randomly seeded in the TiO_2 structures.

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