SYNTHESIS OF CATALYST PARTICLES FOR CARBON FIBER GROWTH
IN A VAPOR GROWN CARBON FIBER REACTOR

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SYMBOLS AND ABBREVIATIONS

\( C_i \)  \hspace{1em} \text{molar concentration of species} \text{ } i

\( C_p \)  \hspace{1em} \text{specific heat of gas}

\( D \)  \hspace{1em} \text{diameter of carbon fiber}

\( D_f \)  \hspace{1em} \text{diameter of filament}

\( D_0 \)  \hspace{1em} \text{initial fiber diameter}

\( F_{k,s} \)  \hspace{1em} \text{volume concentration of component} \text{ } s \text{ in the} \text{ } k\text{-th section}

\( f_{i,s} \)  \hspace{1em} \text{volume concentration of component} \text{ } s \text{ in the} \text{ } i\text{-th discrete size}

\( G \)  \hspace{1em} \text{generation rate of the first discrete size}

\( g_s \)  \hspace{1em} \text{intraparticle component volume fraction probability density function}

\( i_{\text{max}} \)  \hspace{1em} \text{maximum number of discrete size classes}

\( K \)  \hspace{1em} \text{thermal conductivity of gas}
$K_{eq}$ equilibrium reaction rate constant for methane pyrolysis

$K_f$ forward reaction rate constant for methane pyrolysis

$K_s^-$ surface reaction rate constant for fiber lengthening

$K_s^-$ surface reaction rate constant for fiber thickening

$k_B$ Boltzmann constant

$k_{max}$ maximum number of sections

$L$ fiber length

$N$ number concentration of catalyst particles

$n(v,t)$ size distribution function

$P$ gas pressure

$Pr$ Prandtl number

$R$ universal gas constant
Ra  Rayleigh number

Re  Reynolds number

$r_i$  radius of a molecule

$s$  number of components in particle coagulation

$s_{max}$  maximum number of species

$T$  temperature, K

t  time

$u, v$  aerosol volume variables

$\bar{u}_s, \bar{v}_s$  mean volume of component $s$

$v_{1,s}$  volume of first discrete size of component $s$

$\beta$  collision frequency function/integral

$\rho_p$  bulk density of the molecule
$\delta$ logical function: true=1, false=0

$\zeta$ thickness of the fiber filament
CHAPTER 1

INTRODUCTION

1.1 Carbon Fibers

Fiber reinforced composite materials have replaced conventional isotropic materials in many applications because they can be designed to achieve desired properties in any direction. The anisotropy and non-homogeneity of composite materials can be exploited to reduce the weight and material in structures. In composite materials the fibers are arranged to provide stiffness and strength while the matrix material holds the fibers together in a desired geometric form. Fibers are used since materials in fibrous form are generally stronger and stiffer than the bulk form. Fibers may be described as formed material that has a length to diameter ratio of more than 10 with cross-sectional area less than 0.05 mm².

Carbon fibers are extensively used in the fabrication of resin-matrix composites. Carbon fibers consist of at least 92 weight percent carbon, regularly in the non-graphitic stage, that is two dimensional ordering of the carbon atoms in the planar hexagonal networks, but without any measurable crystallographic order in the third direction (c-direction) apart from more or less parallel stacking.
Based on the precursor materials, carbon fibers can be classified as follows:

1. **PAN-based carbon fibers** are obtained from polyacrylonitrile (PAN) precursor fibers by stabilization treatment, carbonization, and possibly final heat treatment at even higher temperature.

2. **Isotropic pitch-based carbon fibers** are carbon fibers obtained from isotropic pitch fibers by stabilization treatment and carbonization.

3. **Anisotropic pitch-based carbon fibers** (MPP-based carbon fibers) are carbon fibers obtained from mesogenic pitch after this has been transformed into mesophase pitch (MPP) during the process of spinning, by stabilization of the spun pitch fibers, carbonization, and final heat treatment at even higher temperature.

4. **Rayon-based carbon fibers** are carbon fibers obtained from rayon precursor fibers by chemical pretreatment and carbonization. They are isotropic carbon fibers and can be transformed into anisotropic carbon fibers with high strength and stiffness by hot stretching above 2800°K.

5. **Gas phase grown carbon fibers** (Vapor Grown Carbon Fibers - VGCF) are carbon fibers grown in hydrocarbon atmosphere with the aid of fine dispersed solid catalysts such as iron or other transition metal particles. They consist of graphitizable carbon and can be transformed into graphite fibers by heat treatment above 2800°K.
The first four types of carbon fibers mentioned above are currently produced commercially, but the fifth type (VGCF) is still in the development stage. The Vapor Grown Carbon Fibers (VGCF), are deposited from hydrocarbon gases on catalyst particles inside a flow reactor. The catalyst particles might be seeded on a substrate surface or be in suspension in the gas flow. Study shows that the properties of VGCF are much superior to the PAN and pitch based carbon fibers.

The history of carbon fibers dates back to more than 100 years when Edison tried to use carbon fiber filament in electrical bulb. But the actual development of carbon fiber started in the sixties, when it was realized that hot stretching of isotropic carbon fibers at graphitization temperature results in high modulus. The high performance of carbon fiber comes mainly from its preferred orientation. In the preferred orientation the strong bonds between the atoms are oriented along the axis of the fibers. There are three different ways to achieve preferred orientation.

1. Hot Working. In this process temperature in the range of 3000ºK is used to stretch the fibers from 50% to 100%. The stretch treatment at the graphitization temperature results in Young’s modulus in the range from 300 to 600 GPa. This method was initially used to produce Rayon-based carbon fibers, but it was abandoned later due to extreme difficulty associated with the process.

2. Prestretching the precursor fiber. This method can be applied to polymer fibers with continuous carbon backbone in which the highly viscous thermoplastic fiber
is stretched. The preferred orientation is stabilized by cross-linkages and cyclization.

3. Orientation during spinning. The third method of orienting fibers preferentially is by a crystallization phenomena during spinning.

Figure 1.1 shows the methods of achieving the preferred orientation. The process steps to produce carbon fibers from PAN are shown in Figure 1.2. There are many

Figure 1.1. Processes for obtaining preferred orientation in conventional carbon fibers (Fitzer, 1990).
process steps involved in the production of conventional carbon fibers as shown in the last two Figures.

The mechanical, electrical, and thermal properties of carbon fibers are given in Table 1. The pitch-based carbon fibers are used in insulation, as fillers in plastics, carbon felts, but have not found use in advanced composite materials because of its low strength and modulus.
Table 1. Properties of carbon fibers.

<table>
<thead>
<tr>
<th>Carbon fiber</th>
<th>Density, g/cc</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Thermal Conductivity W/(m-K)</th>
<th>Electrical Resistivity, ohm-m</th>
</tr>
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<td>VGCF</td>
<td>1.8&lt;sup&gt;2&lt;/sup&gt;</td>
<td>237&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2.92&lt;sup&gt;2&lt;/sup&gt;</td>
<td>500&lt;sup&gt;4&lt;/sup&gt;</td>
<td>310x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>PAN</td>
<td>1.78&lt;sup&gt;1&lt;/sup&gt;</td>
<td>231&lt;sup&gt;1&lt;/sup&gt;</td>
<td>4.0&lt;sup&gt;1&lt;/sup&gt;</td>
<td>8&lt;sup&gt;1&lt;/sup&gt;</td>
<td>120x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Isotropic Pitch</td>
<td>1.16&lt;sup&gt;3&lt;/sup&gt;</td>
<td>55&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.7&lt;sup&gt;3&lt;/sup&gt;</td>
<td>80&lt;sup&gt;3&lt;/sup&gt;</td>
<td>130x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mesophase Pitch</td>
<td>2.0&lt;sup&gt;4&lt;/sup&gt;</td>
<td>160&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.4&lt;sup&gt;4&lt;/sup&gt;</td>
<td>100&lt;sup&gt;4&lt;/sup&gt;</td>
<td>13x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Rayon</td>
<td>1.9&lt;sup&gt;4&lt;/sup&gt;</td>
<td>345&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2.07&lt;sup&gt;4&lt;/sup&gt;</td>
<td>15&lt;sup&gt;4&lt;/sup&gt;</td>
<td>70x10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

2) Tibbetts et al., (1987)
3) Heremans (1985)
4) Heremans et al., (1985)

VGCF obtained from thermal decomposition of hydrocarbons, such as methane (Tibbetts, 1983) and benzene (Koyama, 1972; Endo et al., 1985; Endo et al., 1987) has superior properties and characteristics compared to PAN and pitch-based carbon fibers. Two different methods have been developed to produce VGCF. In the first method fiber is grown on seeded substrate (Koyama, 1972). In the other method fiber is grown on catalyst particles suspended in gas (Endo et al., 1985; Endo et al., 1987). The floating
catalyst method provides higher yield but the fibers grown are much shorter than those grown on seeded substrate.

Carbon fiber reinforced composites are being developed for high specific strength over a wide range of temperatures. However, conventional carbon fibers, such as PAN-based and pitch-based fibers, can not compete with glass fibers in automotive and low cost applications due to their high production costs. High specific stiffness, strength, electrical and thermal conductivity would make carbon fibers a very attractive alternative if production costs could be reduced. Vapor Grown Carbon Fibers (VGCF), produced in a flow reactor by pyrolytic decomposition of hydrocarbon gases, are expected to provide economical and functional advantages in many applications. The VGCF has an atypical microstructure - it has concentric layers of graphitic basal planes parallel to the fiber axis. Unlike an isotropic fiber the physical properties of VGCF along the fiber axis are different from those in the radial direction because of different directional microstructures. The properties of VGCF can be improved significantly through graphitizing by heat treatment. Heat treated VGCF has thermal conductivity of 2000 W/m-K in the longitudinal direction that is much higher than that of copper (390 W/m-K) and aluminum (200 W/m-K). The thermal conductivity of VGCF is 10 - 100 W/m-K in the radial direction. The working temperature for VGCF can be as high as 3000°C in an inert environment, but in air it reduces to about 600°C.

The focus of this dissertation is the analysis and simulation of flow reactors which produce Vapor Grown Carbon Fibers (VGCF) by the pyrolysis of hydrocarbons over
catalytic transition metal particles. A model will be developed to study the formation of catalyst particles and VGCF growth in the flow reactor. The model will be based on the nucleation of particles by collision of molecules of catalyst, which in turn are produced by gas phase chemical reactions. Calculations will be carried out to determine the nucleation rates of the catalyst particles in the mixture, and of the growth rates of the carbon fibers from the catalyst. The model results will be compared with results from experimental VGCF reactors.

1.2 Vapor Grown Carbon Fibers (VGCF)

The effort to grow vapor grown carbon fibers dates back to 19th century when Hughes and Chambers (1889) grew hair-like carbon fibers from hydrogen and methane pyrolyzed in an iron crucible. The technology available at that time could not make the product competitive with the then existing carbon fibers. In 1953, Davis et al. (1953) observed twisted carbon fibers of about 0.01 micron thickness deposited on blast furnace brick works. Iley et al. (1948) grew carbon fibers on quartz substrates at 1200°C from methane, propane, and ethylene feedstock. In 1958 Hillert et al. (1958) grew different shaped carbon fibers by decomposing n-heptane at 1100°C in a silica tube. In some cases they obtained straight fibers of 20 microns diameter and 5 cm long. Koyama (1972) and Koyama et al. (1973) made significant developments in fiber production by decomposing benzene at 1200°C. Endo and his group investigated the relationship
between the fiber structure and the catalytic particles that initiates and helps the growth mechanism (Endo et al., 1983). Physical properties of VGCF have been reviewed in a book by Dresselhaus et al., (1988). Katsuki et al. (1981) grew carbon fibers on many types of catalyst particles by thermally decomposing naphthalene-hydrogen mixture. Tibbetts studied the growth of carbon fiber from methane gas in stainless steel tubes (Tibbetts, 1983) and later in ceramic tubes (Tibbetts et al., 1984) and found that the fiber growth process consists of two disjointed steps, a lengthening step followed by a thickening step. Tibbetts et al. (1987) later modeled the hydrocarbon adsorption and carbon diffusion through the catalyst particles. Benissad et al. also studied methane-hydrogen system and published the conditions (Benissad et al., 1988) of fiber growth and the annealing and melting (Benissad et al., 1988) of the catalyst particles.

Carbon fibers have been grown on catalyst impregnated substrate and on floating catalyst particles. In fibers grown on substrates, gaseous hydrocarbons are thermally decomposed at about 1000°C to produce slender, partially graphitic filaments on metallic catalyst particles which are predominantly iron. If the filaments are exposed to a gas of low carburizing potential a small fraction of these filaments will grow to macroscopic length but will still retain the outside diameter of the initial catalytic particle. The diameter of the most effective catalytic particles (Endo et al., 1983) is less than 10 nanometers which means that the filaments are very slender. The filament diameter can be increased up to 10 micron range by exposing it to a gas of a higher carbon potential to deposit pyrocarbon on the filaments. The fibers thus grown are partially graphitic
because the preferential orientation of the basal planes of pyrocarbon are parallel to the surface (Kaae et al., 1985). Fibers of the best length and graphitic structure may be obtained by flowing a mixture of hydrocarbons and hydrogen over a substrate seeded with catalytic particles and heated to near 1000°C (Tibbetts, 1990). Studies with different catalytic particles such as iron and iron-nickel powder (Endo et al., 1983), ferric nitrate, magnetite particles (Tibbetts, 1985), and complex polymer-based (Katsuki et al., 1981) chars have been published. For best fiber properties the particle diameter should be very small, for particle diameter higher than 15 nm the activity decreases considerably. Particle coagulation during the warm up phase is a critical issue - larger particles will produce undesirable results (Benissad et al., 1988). The optimal conditions for fiber lengthening are not well known. Methane gas pyrolyses to C₂Hₓ in the reactor which is more reactive and dissolve into iron particles. Some favorable conditions for fiber lengthening have been identified by Tibbetts et al. (1987). Tibbetts has shown that 15% (by volume) methane mixed in hydrogen, with reactor temperature around 1000°C, and gas residence time about 20 seconds will grow fibers several cm long in 10 minutes. There will be some pyrolytic carbon present in the fibers grown as above. At all temperatures above 1050°C the fibers will thicken, but good quality pyrocarbon will deposit around 1130°C from feedstock containing 30% methane in hydrogen. The fibers will thicken to 7-10 microns in 2 hours with a gas residence time of about 30 seconds. Fibers grown on substrates resemble furry hair and looks like intertwined mass when
separated from the substrate. There are several inherent problems in growing carbon fibers on substrate:

1. Since this is a batch process it is less attractive to implement it at a commercial level
2. The long residence time required for fiber thickening makes it noncompetitive from a commercial point of view
3. It is difficult to avoid fiber entanglement in this process.

The floating catalyst process was first described by Koyama et al. (1983) and later developed in more detail by Hatano et al. (1985). In the floating catalyst process, the catalytic particles are either added to the feedstock or are obtained by thermally decomposing an organometallic compound in the reactor. The fiber lengthening and thickening process can be controlled by adjusting the carbon potential in the gas. The fibers grow as they flow along the gas stream inside the reactor and are collected at the outlet. The gas phase process can be operated as a continuous process and the reactor parameters can be varied to produce fibers of varying yield, length, diameter, and physical properties. Fiber diameters are very uniform, but the method can not produce fibers as long as those grown on substrates.

The thickening of the filament takes place by chemical vapor deposition (CVD) of carbon on the tubular filament in a cylindrically symmetric manner. Figure 1.3 shows the
cross-section of a VGCF which resembles concentric annular rings of onion rings. In this unique fibril structure the graphitic basal planes are highly preferentially oriented (Oberlin et al., 1976). The morphology of PAN and pitch-based carbon fibers are quite different from that of VGCF. VGCF has superior strength normal to its axis and higher torsional stiffness (due to its annular structure) than the pitch-based fibers which have graphitic planes perpendicular to the fiber axis. Heat treatment of carbonaceous materials
can improve their graphitic ordering. Isotropic PAN and pitch-based fibers graphitize very poorly, but VGCF are highly graphitizable; and when heated to over 2900°C, the graphitic structure of VGCF becomes superior to any known fiber (Endo et al., 1976).

The stress-strain plot of a typical VGCF is shown in Figure 1.4. The apparent modulus increases with the increase in strain. There can be as much as 20% increase in

Figure 1.4. Stress versus strain curve for a Union Carbide T-300 fiber and a vapor grown graphitic fiber which has been exposed to a maximum temperature of 1130°C (Tibbetts, 1990).
tensile modulus due to strain induced stiffening (Beetz et al., 1983). The improvement in tensile modulus with increased strain results from improved orientation which is attributed to strain induced reorientation of the graphitic basal planes. Figure 1.5 shows the variation of stiffness of fibers with diameter (Tibbetts et al., 1987) for one batch of VGCF. Fiber diameter under 10 microns, an appropriate size for use with most composites, has stiffness in the range of 188 to 286 GPa. It is interesting to note that the fibers grown simultaneously on a substrate in the reactor can have different structures and

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Figure 1.5. Young’s modulus of vapor grown carbon fiber as a function of fiber diameter. The maximum temperature in the reactor was 1130°C (Tibbetts, 1990).
properties. The fibers grown in the hottest zone of the reactor thickens at a faster rate than those near the entrance and the exit of the reactor. The higher stiffness at a smaller fiber diameter can be attributed to the fact that carbon deposition at a slower rate in a CVD process results in a better fiber properties (Kaee, 1985).

During heat treatment, VGCF develops orientation at a much lower temperature than both PAN and pitch-based carbon fibers. Like the modulus of VGCF, the tensile strength also decreases with the fiber diameter which is shown in Figure 1.6. The tensile strength is about 2.92 GPa for fibers of 7.5 micron diameter.

Figure 1.6. Tensile strength of VGCF as a function of fiber diameter (Tibbetts, 1990).
Conventional carbon fibers generally fail in brittle fracture and may even explode in the microtensilometer, but VGCF heat-treated above 1130°C will graphitize to such an extent that the failure is usually non-catastrophic. The brittle fracture of PAN and pitch-based carbon fibers are compared with “pull-out” failure of VGCF in Figure 1.7.

![Graph showing fracture behavior of VGCF and other carbon fibers](image-url)

Figure 1.7. Fracture behavior of VGCF as prepared and heat treated at 2200°C compared with that of PAN and pitch based carbon fibers (Tibbetts, 1990).

Resistance of carbon fiber to oxidation is determined by the properties and orientation of pyrocarbon from which the fibers are formed. Figure 1.8 shows that VGCF (as grown)
has more resistance than PAN-based fibers heat-treated at 1000°C. VGCF, when heat treated, has improved resistance due to increased graphitization and improved basal plane orientation.

Figure 1.8. Thermograph for the oxidation of various fibers in 50 cc/min. of flowing air at a heating rate of 5°C per minute. The VGCF are as grown at 1050°C and heat treated at 2800°C (Benissad et al., 1988).

Electrical resistivity of VGCF as measured by Heremans (1985) are plotted against temperature in Figure 1.9. The plot includes the resistivity of fibers heat treated at different temperatures starting from 2000°C to 3000°C. The VGCF grown at 1100°C has
resistivity $2 \times 10^{-5}$ ohm-m which is virtually independent of temperature. The graphitization due to heat treatment reduces heavier hydrocarbons, and thereby reduces resistivity.

Figure 1.9. Model (solid lines) and experimental (points) values of electrical resistivity of VGCF heat treated at different temperatures (Heremans, 1985).

The thermal conductivity of vapor grown carbon fiber was measured and reported by Heremans and Beetz (1985). High thermal conductivity of VGCF might be the most
compelling reason for its application. Thermal conductivity of VGCF as-grown and heat-treated at 3000°C are shown in Figure 1.10. The thermal conductivity of heat treated VGCF can be as high as 3000 W/m-K, approaching that of single crystal graphite.

Figure 1.10. Temperature dependence of the thermal conductivity of as grown (open circles) and 3000°C heat treated (solid circles) VGCF (Heremans et al., 1981).
VGCF can not compete with continuous fibers in demanding structural applications such as in aeroplane frames, but can be used to fabricate chopped fiber composites using ceramics, plastic, metals and cement matrices. Figure 1.11 shows the possible areas of application of VGCF and its properties. In electronic industry VGCF find application as
a heat sink for their exceptionally high thermal conductivity. VGCFs are also suitable to be used in plastic composite for electromagnetic shielding because of their high electrical conductivity, particularly after heat treatment. A substantial improvement of electrical conductivity of VGCF can be achieved by intercalating electron donor or acceptor atoms into the graphitic lattice. The electrical conductivity of VGCF has been improved recently by intercalating AsF$_5$ into heat treated VGCF to a value greater than that of copper. This high electrical conductivity material has a possibility of finding usage in aerospace applications. The price and availability of VGCF are the factors that will determine the extent of its use. It is expected that a successful technology will emerge in the near future that will be able to produce VGCF at a low cost from natural gas.
CHAPTER 2

VGCF REACTOR

The history of growing carbon fibers from hydrocarbon gases is more than 100 years old (Hughes and Chambers, 1889), but the detailed mechanisms of fiber formation and growth are still not completely understood. Since then, there have been many attempts to explore the underlying principles behind VGCF production. Endo et al. (1983) have investigated the relationship between the fiber structure and the catalytic particles that initiate and enhance the growth of fibers.

2.1 Catalyst Particle - Effect of Sulfur

The catalyst particles produce very small carbon fibers from the deposited carbon. A typical length is about 25 micron, and the initial diameter of the fiber is approximately equal to the catalyst diameter - about 0.1 micron. The fibers grow thicker by chemical vapor deposition (CVD), and the final thickness is of the order of 1/2 micron. The size of the catalyst particle will determine the diameter of the carbon fiber. Consequently the catalyst size is also an important parameter for the VGCF process. The yield of carbon fibers also depends on the number or volume concentration of the catalyst in the gases.
The determination of catalyst size, concentration, and composition are the objectives of this study.

Carbonaceous gases decompose at an elevated temperature in the presence of metallic catalyst particles to produce thin and long carbon filaments from the particles. The filament grows out from the catalyst particle that has a diameter approximately equal to that of the catalyst particle. The catalytic growth lengthens the filament as a hollow cylinder. The deposition of carbon on the sides of the filament causes thickening and radial growth of the vapor grown carbon fiber. Transition metals such as iron, nickel, copper, palladium can be used as catalyst particles, but iron is used most commonly. The iron particles can be obtained from the solution of iron salts or iron organometallics, such as Fe(NO$_3$)$_3$·9H$_2$O, Fe(C$_5$H$_5$)$_2$, Fe(CO)$_5$, Fe$_2$(SO$_4$)$_3$, Fe(NO$_3$)$_3$·9H$_2$O+KOH etc. The carbon in the fiber can be obtained from carbonaceous gases such as methane, acetylene, ethylene, benzene, natural gas etc. The catalyst particles adsorb and decompose the carbon-containing gas on their surface. It has been suggested (Tibbetts, et al., 1993) that carbon dissolves and diffuses through catalyst particle from the hotter leading surface (where exothermic reaction of hydrocarbon decomposition takes place) to the colder rear surface where it precipitates from the solution (which is an endothermic reaction). The precipitation of dissolved carbon increases the filament length which continues to grow as long as the catalyst particle is active. Catalytic filament growth ceases when the leading edge of the particle is encapsulated by carbon deposition that prevents further
hydrocarbon decomposition or if the catalyst particle loses its catalytic properties due to the chemical transformation.

Figure 2.1 shows a schematic of a VGCF reactor. Hydrocarbon gas such as methane is introduced along with Fe(CO)$_5$ vapor into a cylindrical tube inside a furnace heated to 1100°C - 1150°C. Along with these reactants, H$_2$S gas is also added. The decomposition of Fe(CO)$_5$ produces iron particles. The iron particles are suspended in the gases, and are carried along with the flowing gases. The H$_2$S gas decomposes at a different temperature than that of Fe(CO)$_5$, and sulfur is then incorporated into the iron particles.
The sulfur fraction in the catalyst particle is a critical parameter that determines the activity of the catalyst particle. Figure 2.2 shows scanning electron micrographs of VGCF grown with different hydrogen sulfide flow rates with the precursor gas. It can be observed from Figure 2.2 that with a high level of hydrogen sulfide, there are few fibers with much carbon soot. Good quality fibers are obtained with an appropriate amount of hydrogen sulfide.

The incorporation of a proper quantity of sulfur in the iron catalyst particle enhances the carbon fiber growth by lowering the melting point of the catalyst. It is suspected that the liquid catalyst particles can dissolve and decompose the vapor phase deposition species (hydrocarbons) more efficiently (Wagner et al., 1965) to produce the fiber filaments at a fast rate. The phase diagram of Fe-S (Kubaschewski, 1982), shown in Figure 2.3, explains the mechanism of catalyst enhancement by sulfur inclusion. The catalyst particle can enable rapid fiber growth in the VGCF reactor because the gas temperature in the reactor exceeds the eutectic temperature (988°C) of the Fe-S system for a sulfur content of 52 atomic percent. Finally, methane decomposes in the reactor, and carbon is deposited onto the iron catalyst particles.
Figure 2.2. Scanning electron micrographs of typical VGCF fibers grown with residence time of 55 seconds and hydrogen sulfide flow rates of: a) 0, b) 5.9 cm$^3$/min, c) 22 cm$^3$/min. (Tibbetts et al., 1993).
2.2 Phases of The Current Study

Even though the Pyrograf reactor was developed at General Motors approximately twenty years ago, a detailed analysis of the process, including heat transfer and fluid flow,
catalyst particle formation and growth, and fiber growth has not been done so far. The developments of this reactor have been based on experimental research and empirical formula based on experiments. Therefore, there are three phases of this proposed study.

1) CFD Modeling: Modeling the fluid flow field and the temperature field inside the Pyrograf reactor is carried out by using a commercial finite element code - FIDAP. Simple temperature profiles verified by the CFD modeling will be used in the subsequent particle dynamics (catalyst particle formation and growth) and CVD (fiber formation and growth) calculations because the processes are strongly temperature dependent.

2) Catalyst Formation and Growth: Investigation of the catalyst particle composition and growth inside the Pyrograf reactor will be done by using particle dynamics theory. The catalyst particle formation and growth is the most critical aspect of the fiber production process because the catalyst particle size is an important factor in determining the fiber diameter and the catalyst particle composition determines the catalytic effect for the fiber lengthening process. A numerical solution will be developed to calculate the catalyst particle size, concentration, and composition from given precursor gas concentrations. Calculations have been carried out by using a simple temperature profile obtained from CFD investigation. The
diameter of the catalyst particles will then be used as the filament diameter.

Initially calculations will be carried out with only the iron particles in the reactor (single species) and compared with experimental results. For the single species calculations, a small amount of Fe(CO)$_5$ will be added with the inert carrier gas (He gas is the carrier gas). Two species calculations are to be carried out to determine the composition of the catalyst particles (iron and sulfur). The two species calculations relate the ratio of H$_2$S and Fe(CO)$_5$ in the precursor gas to sulfur fraction in the catalyst.

3) Carbon Fiber Growth: A preliminary study of the carbon fiber formation and growth processes inside the Pyrograf reactor is done by applying CVD theory. The kinetics of fiber lengthening is different from the classical CVD processes - the effect of the catalyst particle is to lengthen the fiber at a much faster rate than the thickening process. The fiber lengthening process continues until the catalyst particle is buried by carbon deposition or it gets poisoned by the chemical reactants in the reactor. The fiber thickens by carbon deposition on the filament surface.
2.3 Pyrograf Reactor

Two Pyrograf reactors will be considered in this study. The first one is a reactor at the General Motors Research and Development Center (GM Reactor) and the second one is a hypothetical production scale reactor (scaled-up reactor). The GM Reactor is to be used as the only source of experimental data. The GM reactor has been simulated to determine the temperature profiles and particle and fiber growth, and these results will be compared with experimental data. The temperature fields will be calculated in the scaled-up reactors to investigate the flow regimes in larger reactors. The VGCF reactor model consists of a mullite tube which is heated externally by a resistive heating furnace. The GM Reactor is 91.4 cm long and 1.45 cm in diameter and the scaled-up reactor is 2.311 m long and 13.6 cm in diameter. Figure 2.4 shows the schematic diagram and the temperature boundary conditions for the GM Reactor. Similar temperature boundary conditions have been applied to the scaled-up reactor.

Iron pentacarbonyl and hydrogen sulfide are added to the precursor gas to produce the catalyst nuclei inside the reactor by chemical reaction at elevated temperature. In the first phase of the process, iron and sulfur molecules are produced by decomposition of iron pentacarbonyl and hydrogen sulfide. The molecules collide with each other, thereby producing a catalyst nuclei. These nuclei grow by collision. Methane pyrolysis and chemical vapor deposition of the pyrolyzed hydrocarbons take place at a later phase, and carbon is deposited on the nuclei.
The growth of fibers by chemical vapor deposition (CVD) is determined by the reactor temperature, reactant concentrations, and the residence time. The residence time is inversely related to the gas flow velocity, and is of the order of 50 seconds for fiber production. However, the catalyst particle formation occurs very early in the process and is completed within approximately one second.

Figure 2.4. Schematic diagram of the GM Reactor and the temperature boundary condition along the reactor wall (not drawn to scale).
For catalyst particle production in the GM Reactor described above, the residence time is of the order of 1 second, the Reynolds number is about 60, and the Rayleigh number is about 600. This implies that the thermal entrance length effect is small, and that buoyancy effects can be neglected. The temperature history is to be taken from the FIDAP simulations by averaging the simulation temperature results and used in the aerosol and CVD calculations.

The calculations will be carried out for the formation of catalyst particles that contain iron and sulfur. The formation and growth history of the catalyst particles will be compared with experiments carried out in the GM Reactor. The fiber growth history will be examined on the basis of experimental data from the GM reactor.

Tibbetts (1983) studied the growth of carbon fiber from methane gas in stainless steel tubes and later in ceramic tubes. From these studies it was determined that fiber growth process consists of two separate steps - axial growth or a lengthening process followed by thickening due to the classical chemical vapor deposition (CVD) process. In the second step, fiber grows in the radial direction by CVD, thereby producing a thicker fiber. The TEM of a VGCF fiber is shown in Figure 2.5 (Tibbetts et al. 1993). There are two distinct regions in Figure 2.5(a) - the brighter central part is the fiber filament and the darker outer part is the pyrolytic carbon that is deposited by CVD on the filament. The catalyst particle can be seen at the tip of the fiber - this is the source of filament growth. The fiber filament has a rather crystalline structure that can be distinguished from the less
Figure 2.5. (a) TEM of a VGCF fiber showing the buried catalyst particle, filament, and the outer carbon layer. (b) TEM of the transverse sectional view of a VGCF showing the cylindrical symmetry of the filament and the outer pyrocarbon (Tibbetts et al. 1993).
ordered carbon deposited in concentric layers from the vapor phase. A transverse cross sectional view of a VGCF is shown in Figure 2.5(b) which also shows the darker crystalline filament surrounded by the less crystalline pyrocarbon.

As mentioned earlier, addition of sulfur is very important in improving the catalytic effect of the particles. A critical step in the production of VGCF is the nucleation of catalyst particles in the gas phase. The catalyst particles determine the characteristics of the fiber. The primary objective of this investigation is to model the processes of catalyst particle formation in the reactor. The analysis is based on the particle dynamics theory (Gelbard et al., 1979) applied to the analysis of aerosols (Biswas et al., 1997), in which particles are formed by collisions of single molecules producing molecular clusters, and the molecular clusters grow by inter-particle collisions. The limitation of the above mentioned work (Biswas et al., 1997) is that the composition of the particle can not be determined. However, the composition of the catalyst particles is a critical parameter in the performance of the VGCF reactor. Therefore, a more sophisticated model has been developed that can track the catalyst composition (iron and sulfur) as the particles nucleate and grow. The results from the particle collision model provide information on the particle sizes, number or volume concentration, and composition of the catalyst particles. These results are then used to determine the dimensions of the fiber. The analysis have been applied to the GM reactor and the results are compared with experimental data.
CHAPTER 3

THEORETICAL MODEL

3.1 CFD Simulations

The flow and the temperature fields in the Pyrograf reactor have been calculated by using a commercial CFD code FIDAP. FIDAP is a finite element (FEM) code. Before performing the reactor simulations, a theoretical analysis was carried out to find the effects of natural convection. Following the treatment of Bejan (1984) let us define a non-dimensional parameter $G$ to determine the natural convection effects in the reactor.

\[
G = \frac{Ra^{1/4}}{Re^{1/2} Pr^{1/3}}
\]

where,

$Pr$ = Prandtl number

$Ra$ = Rayleigh number

$Re$ = Reynolds number
When the value of non-dimensional parameter $G$ is much larger than unity it implies natural convection dominated flow and a value much less than unity implies forced convection dominated flow. The GM reactor has a diameter of 1.45 cm and a length of 91.4 cm. The length of the base scaled up reactor is 2.311 m long and has a diameter of 13.6 cm. For nominal operating conditions of the GM reactor and the scaled-up reactor, the values of $G$ are 0.7 and 3.1 respectively. The values of $G$ implies that, for the scaled up reactor, natural convection will dominate the flow. A complete analysis of the reactor flow including the natural convection effect would require a complex 3-D analysis. Since the major focus of this study is on the catalyst formation, it is preferable to carry out a simpler axisymmetric flow analysis. The GM Reactor has been modeled as a axisymmetric problem and this will be justified later. The flow has been treated as a variable density flow due to the high temperature gradient along the flow. The variation of the physical and thermal properties of the fluid is significant in the reactor, and hence the temperature dependent properties of the gas have been included in the simulation. The properties of methane have been used in the simulations since it comprises about 99 percent of the inlet gas.

The steady state reactor simulation involves simultaneous solution of the following three coupled equations.

1) Mass Conservation Equation

$$\nabla \cdot \rho \mathbf{u} = 0 \quad (3-1.a)$$
2) Momentum Conservation Equation

\[ \nabla \cdot (\rho \mathbf{uu} - \mu \nabla \mathbf{u}) = -\nabla P \quad (3-2.a) \]

3) Energy Conservation Equation

\[ \nabla (\rho u C_p T - K \nabla T) = 0 \quad (3-3.a) \]

In the above conservation equations \( \rho \) is the density, \( \mu \) is the viscosity, \( K \) is the thermal conductivity, \( C_p \) is the specific heat, \( u \) is the velocity, \( P \) is the pressure, and \( T \) is the temperature of the gas. The conservation equations are coupled since the gas properties are temperature dependent, and hence they need to be solved simultaneously. The temperature dependent properties of gas make the system of equations nonlinear. The nonlinearity of the governing equations together with the high temperature gradient inside the reactor make it difficult to obtain a converged solution unless the equations are non-dimensionalized. There are some significant advantages from dimensionless formulation. The dimensionless parameters obtained by scaling the fundamental variables with respect to typical values provide a measure of relative contribution of various terms in the governing equation and identifies the dominant physical phenomena of the process. The benefit of nondimensionalization is derived from the fact that it reduces the order of magnitude differences among the terms of an equation and hence increases the convergence rate.
The nondimensionalization of the above conservation equations have been carried out as follows.

\[ u^* = \frac{u}{U} \quad (3-1-1) \]

\[ x^* = \frac{x}{L} \quad (3-1-2) \]

\[ T^* = \frac{T - T_o}{T_{max} - T_o} \quad (3-1-3) \]

\[ P^* = \frac{P}{U^2 \rho_o} \quad (3-1-4) \]

\[ \rho^* = \frac{\rho}{\rho_o} \quad (3-1-5) \]

\[ \mu^* = \frac{\mu}{\mu_o} \quad (3-1-6) \]

\[ K^* = \frac{K}{K_o} \quad (3-1-7) \]
In the above transformations the superscript "*" denotes dimensionless parameter. On the right hand side the variables in the numerator are the fundamental variables and the ones in the denominator are the scale values. The variables with subscript "0" represent the value of the variable at a reference temperature. The reference temperature used in the CFD simulation is 1000°K. The reference velocity $U$ is the gas velocity inside the reactor at the reference temperature, and $L$ is the length of the reactor. The following nondimensional conservation equations are obtained by using the dimensionless parameters in the conservation Eqns. (3-1.a) through (3-3.a).

1) Nondimensional Mass Conservation Equation

$$\nabla \cdot \rho^* = 0$$  \hspace{1cm} (3-1.b)

2. Nondimensional Momentum Conservation Equation

$$\nabla \cdot (\rho^* u^* \mu^* - \frac{1}{Re_L} \mu^* \nabla u^* ) = -\nabla P^*$$  \hspace{1cm} (3-2.b)
3. Nondimensional Energy Conservation Equation

\[ \nabla (\rho^* u^* C^* T^* - \frac{1}{P_e L} K^* \nabla T^*) = 0 \]  \hspace{1cm} (3-3.b)

where, \( P_e L = \frac{\rho_o C_p U L}{K_o} \) is the Peclet number and \( R_e L = \frac{\rho_o U L}{\mu_o} \) is the Reynolds number based on the reactor length \( L \).

Comparing the nondimensional conservation equations with the respective dimensional equations it can be determined that the effective viscosity and effective thermal conductivity of gas are \( \frac{\mu^*}{R_e L} \) and \( \frac{K^*}{P_e L} \) respectively.

3.2 Catalyst Nucleation Model

The focus of this dissertation is to examine the formation and growth of iron catalyst particles by a particle collision model and to theoretically determine the size, composition, and volume concentration of the catalyst in the gases. The gas phase decomposition of iron pentacarbonyl and hydrogen sulfide produces molecules of catalyst. The nucleation process consists of catalyst particle growth by collisions of these molecules, resulting in larger clusters, which then sinter to a larger particle. The process
of creating clusters by sticking together is known as coagulation. The size of the catalyst nuclei can also increase due to the condensation or reaction of gaseous phase on the solid nuclei; however, such processes will not be included in this model for the lack of kinetic data.

In this analysis the particles will be assumed to be spherical. Since the catalyst particles are not truly spherical, the simulation results will be compared with an equivalent dimension for the particles produced in the experiment. It should be noted that the measurement techniques for particles typically provide an equivalent diameter for the particle. Non-spherical particles are difficult to characterize by common measurement techniques.

Figure 3.1 shows a schematic representation of the particle dynamics approach for the catalyst nucleation process. Molecules and molecular clusters of iron which are produced as tiny particles by decomposition of iron pentacarbonyl collide with each other due to Brownian motion, and then sinter together to form a single particle. The Brownian motion of particles decreases rapidly with increase in their mass. Therefore, the collision frequency of these particles also decreases with increase in the particle size.
Figure 3.1. Particle dynamics model for catalyst nucleation.

The collision frequency of particles has been studied extensively and a general formula for the collision frequency function of spherical particles (Fuchs, 1964) is shown below.

$$\beta(u,v) = \frac{6k_BT_{i,s}}{\rho_{p,s}} \left[ \frac{1}{i} + \frac{1}{j} \right] \times (i^{1/3} + j^{1/3})^2$$ \hspace{1cm} (3-4)

where,

- $k_B$ is Boltzmann's constant
- $T$ is the absolute temperature of the gas-particle system
The volume conservation equation for a single species of particles as they undergo collision and coagulation is described by the General Dynamic Equation (GDE) (Fuchs, 1964). There are two approaches to particle dynamics - discrete approach and continuous approach. The discrete approach describes the formation of smaller clusters more accurately such as the initial formation of new particles from the homogeneous nucleation of molecules. On the other hand, the continuous approach is more suitable to systems of broad particle size spectrum which is numerically intractable by the discrete method. The continuous approach, however, can not represent the dynamics of small clusters accurately. The objective of this dissertation is to combine both the discrete and continuous formulations (discrete-sectional model) to model multi-component particle coagulation.
A schematic representation of the numerical model for a single species would be a series of particle size classes as shown in Figure 3.2. The solid molecules formed by chemical reaction go into discrete size class 1. Two single molecules of size class 1 colliding with each other will form a cluster of two molecules and thereby will be transferred to discrete size class 2. The collision and subsequent sintering of a particle of size class 1 with one from size class 2 will result in removal of one member from each size class and add one in discrete size class 3. This is called the discrete coagulation formulation for particle dynamics (Wu et al., 1988). The particle-particle collision can be between any two size classes and there are also possibilities of collision involving particles within a size class. Since a typical catalyst particle would have millions of molecules, it is obvious that the
calculations become intractable as the number of size classes increase. To reduce the computational effort, clusters larger than 10 molecules will be treated by continuous distribution. The continuous particle size domain will be divided into range of particle sizes known as “sectional size class”. Instead of each size class containing uniform clusters with a specific number of molecules, sectional size classes are set up containing a range of sizes. For example, the first sectional size class (size class 11) was allowed to have particles with 11 to 15 molecules, whereas the second sectional size class (size class 12) had particles with 16 to 25 molecules.

Interaction of particles in each of the size classes and in the combination of the discrete and sectional particle classes comprises the discrete-sectional model in particle dynamics (Wu et al., 1988). In essence, the discrete-sectional model is the theory of volume conservation for molecules and molecular clusters as they undergo collision and also grow by condensation or chemical reaction.

To reduce computational complexity, inter-species coagulation in the discrete size classes will not be allowed. This is not a very severe limitation since the species (iron and sulfur) formation do not start at the same time (the decomposition temperatures of iron pentacarbonyl and hydrogen sulfide are different). Therefore, there will be two different discrete size classes - one for each of the species. The interaction between iron and the sulfur particles are, however, allowed in all sectional size classes.
3.3 Discrete-Sectional Particle Dynamics Model

3.3.1 Discrete Distribution Model

In the discrete distribution approach the number of monomers in all particles are tracked exactly. Let the particle volume distribution function $q(v,t)$ and the particle size distribution function $n(v,t)$ be functions of particle volume $v$ and time $t$. The particle size distribution function $n(v,t)$ is a frequency distribution function which represents the number of particles of volume $v$ in particle size dimension. The particle size distribution function for discrete particle representation is shown in Figure 3.3. The relationship between particle volume distribution function and particle size distribution function is given below in Eqn. (3-5).

$$q(v,t) = v.n(v,t) \quad (3-5)$$

For discrete representation the particle volume distribution function is same as the volume concentration $f(v,t)$ of particles in the carrier gas.

$$f(v,t) = q(v,t) = v.n(v,t) \quad (3-6)$$

The coagulation rate between particles of size $v_i$ (containing $i$ monomers) and $v_j$ (containing $j$ monomers) in discrete method is given by $\beta(v_i,v_j)n(v_i,t)n(v_j,t)$
where,

\[ v_i = i \cdot v_{1,s} \]
\[ v_j = j \cdot v_{1,s} \] (3-7)

The volume of a monomer is denoted by \( v_{1,s} \) where the subscript \( s \) represents the \( s \)-th component in a multi-component coagulation. Now the rate of formation of particle volume in discrete size class \( m \) (\( m \geq 2 \)) from the coagulation of smaller particles is given by the following expression.

![Figure 3.3. Particle size distribution function for a discrete model.](image)
formation rate \(= \frac{1}{2} \sum_{i+j=m} \beta(v_i, v_j).n(v_i, t).n(v_j, t).(v_i + v_j) \) \hspace{1cm} (3-8)

where,

\[ v_i + v_j = v_m \] \hspace{1cm} (3-9)

The above formation rate Eqn. (3-8) has been multiplied by \(\frac{1}{2} \) because the collision between any two particles would have been accounted twice without it. Using Eqn. (3-6) the rate of formation of particle volume can be expressed in terms of particle volume itself instead of the size distribution function \(n(v, t)\) as follows.

\[ n(v_i, t) = \frac{f_{i,s}(v_i, t)}{v_i} \] \hspace{1cm} (3-10)

where subscript \(i\) represents the \(i\)-th discrete size class and \(s\) represents monomers of component \(s\) in the particle. Therefore, the formation rate of particle volume in discrete size class \(m\) can be written as follows.

\[ \text{formation rate} = \frac{1}{2} \sum_{i+j=m} \beta(v_i, v_j).\left(\frac{v_i + v_j}{v_i.v_j}\right)f_{i,s}(v_i, t).f_{j,s}(v_j, t) \] \hspace{1cm} (3-11)
The above equation can be rewritten to express the formation rate of discrete particles in size class $i$ as:

$$\text{formation rate} = \frac{1}{2} \sum_{j=1}^{i-1} \beta(v_j, v_{i-j}) \left( \frac{v_j + v_{i-j}}{v_j v_{i-j}} \right) f_{j,s}(v_i,t)f_{i-j,s}(v_{i-j},t)$$  \hspace{1cm} (3-12)

The above rate equation can be written in a more compact form

$$\text{formation rate} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{j,i,j,s} f_{j,s} f_{i-j,s}$$  \hspace{1cm} (3-13)

by using Eqn. (3-6) and defining a coagulation coefficient as follows:

$$\beta_{j,i,j,s} = \beta(iv_{1,s}, jv_{1,s}) \frac{v_{1,s}(i+j)}{(iv_{1,s})(jv_{1,s})}$$  \hspace{1cm} (3-14)

The removal rate of particle volume from size class $i$ due to collision between size $i$ particles with other discrete size classes is:

$$\text{removal rate} = \sum_{j=1}^{i-1} \beta(v_i, v_j) n(v_i,t)n(v_j,t)v_i$$  \hspace{1cm} (3-15)
Using the same procedure as the formation rate, the removal rate of size class \( i \) particles can be written in a compact form as follows.

\[
\text{removal rate} = f_{i,s} \sum_{j=1}^{\text{max}} 2 \beta_{i,j,s}^{DD} f_{j,s} \tag{3-16}
\]

where, the coagulation coefficient for the particle removal from discrete size class \( i \) is:

\[
2 \beta_{i,j,s}^{DD} = \beta(i_{i,s}, j_{i,s}) \frac{i_{i,s}}{(i_{i,s})(j_{i,s})} = \beta(i_{i,s}, j_{i,s}) / (j_{i,s}) \tag{3-17}
\]

The particles in the first discrete size class are formed from gas phase chemical reaction inside the reactor at a rate \( G_s \). The discrete particle dynamics equations for the first and higher size classes are given below by Eqns. (3-18) and (3-19) respectively.

\[
\frac{df_{i,s}}{dt} = G_s - f_{i,s} \sum_{j=1}^{\text{max}} 2 \beta_{i,j,s}^{DD} f_{j,s} \tag{3-18}
\]

\[
\frac{df_{i,s}}{dt} = \frac{1}{2} \sum_{j=i+1}^{\text{max}} \beta_{i,j-1,s}^{DD} f_{j,s} f_{i,j-1,s} - f_{i,s} \sum_{j=1}^{\text{max}} 2 \beta_{i,j,s}^{DD} f_{j,s} \tag{3-19}
\]
3.3.2 Continuous Distribution Model

In continuous distribution the particle size domain is divided into \( k_{\text{max}} \) number of sections and the total number of species to be conserved during coagulation is \( s_{\text{max}} \) in a multi-component model. Therefore, the number of equations to be solved simultaneously in each time step is \( (k_{\text{max}}, s_{\text{max}}) \).

In continuous distribution model (Friedlander, 1977) the particle size distribution function \( n(v,t) \) is defined such that \( n(v,t)dv \) is the number concentration of particles in the size range \([v, v+dv]\) at time \( t \). The total particle volume concentration \( F_k(t) \) per unit volume of carrier fluid in any arbitrary section \( k \) at time \( t \) can be represented by the area under the plot of \( vn(v,t) \) versus \( v \) as shown in Figure 3.4. Mathematically, it can be expressed as

\[
F_k(t) = \int_{v_{k-1}}^{v_k} vn(v,t)dv = \sum_{s=1}^{s_{\text{max}}} F_{k,s}(t) \quad (3-20)
\]

where, \( F_{k,s} \) is the volume concentration of component \( s \) in section \( k \), \( v_{k-1} \) and \( v_k \) are the smallest and the largest particle sizes in section \( k \).

In multi-component sectional approach, the conservation equations are derived by determining the rate of addition and removal of each component in each section. The
particle interaction will be limited to binary coagulation between particles in the volume ranges \([u, u+du]\) and \([v, v+dv]\). The rate of collision between such particles is given by

\[
\text{collision rate} = \beta(u,v)n(u,t)n(v,t)du dv
\]  

(3-21)

The total rate of coagulation for all the particles in sections smaller than \(k\) is given by

\[
\text{coagulation rate} = \frac{1}{2} \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \beta(u,v)n(u,t)n(v,t)du dv
\]  

(3-22)

Figure 3.4. Particle size distribution function in sectional approach.
The \(1/2\) in the above expression is due to the fact that \(\beta(u, v) = \beta(v, u)\) for binary collisions. Particle addition in section \(k\) due to the above coagulation will however, take place if the particle formed is in the volume range \([v_{k-1}, v_k]\).

The particle addition rate in section \(k\) from smaller particle coagulation can be obtained by introducing Kronecker delta function \(\delta\) such that,

\[
\delta(v_{k-1} < (u + v) < v_k) = \begin{cases} 
1, & v_{k-1} < (u + v) < v_k \\
0, & \text{otherwise}
\end{cases}
\]  

(3-23)

Therefore, the volume flux rate into section \(k\) from coagulation of smaller particles is,

\[
\text{volume flux rate} = \frac{1}{2} \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(v_{k-1} < u + v < v_k)(u + v)\beta(u, v)n(u, t)n(v, t)du dv
\]

(3-24)

The term \((u+v)\) in the integrand is added to account for the total volume of incoming particles in section \(k\) from coagulation of smaller section particles. In multi-component model, the volume flux of component \(s\) in section \(k\) is the sum of the volumes of component \(s\) in the colliding particles. The composition of the particles in same section will not be necessarily the same and in general the composition may not be a unique
function of particle size. Therefore, let us define a intra-particle component volume
fraction probability density function \( g_s(v, \theta_s) \), where \( 0 < \theta_s < 1 \), and \( g_s(v, \theta_s) d\theta_s \) is the
time dependent fraction of particles in the volume range \([v, v+dv]\) with a volume fraction
of component \( s \) in the range of \([\theta_s, \theta_s + d\theta_s]\). Therefore,

\[
\int_0^1 g_s(v, \theta_s) d\theta_s = 1
\]

(3-25)

and \( g_s(v, \theta_s)n(v,t)dvd\theta_s \) is the number concentration of particles in the volume range
\([v, v+dv]\) with a volume fraction of component \( s \) in the range \([\theta_s, \theta_s + d\theta_s]\). Now, for
particles in the size range \([v, v+dv]\), the volume concentration of component \( s \) is given by

\[
\text{volume concentration of component } s = \left\{ \int_0^1 \nu \theta_s g_s(v, \theta_s) d\theta_s \right\} n(v,t)dv
\]

(3-26)

The volume flux of component \( s \) into section \( k \)

\[
= \frac{1}{2} \int_{v_{k-1}}^{v_k} \int_{v_{k-1}}^{v_k} \delta(v_{k-1} < u + v < v_k) \left\{ \int_0^1 \int_0^1 (u\gamma_s + v\theta_s) g_s(u, \gamma_s) g_s(v, \theta_s) d\gamma_s d\theta_s \right\} \beta(u,v)n(u,t)n(v,t)dudv
\]

(3-27)

The above Eqn. (3-27) can be reduced to the following form by using the property of
\( g_s(v, \theta_s) \).
The volume flux of component $s$ into section $k$

$$\frac{1}{2} \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(v_{k-1} < u + v < v_k) \left\{ u \int_0^{\gamma_s} g_s(u, \gamma_s) d\gamma_s + v \int_0^{\theta_s} g_s(v, \theta_s) d\theta_s \right\}$$

$$\beta(u, v)n(u, t)n(v, t) dudv$$

(3-28)

In the volume ranges $[v, v+dv]$ and $[u, u+du]$ a mean volume of component $s$ for all particles can be defined as,

$$\bar{v}_s = \int_0^{v_0} v \theta_s g_s(v, \theta_s) d\theta_s = \int_0^{\theta_s} \bar{v}_s g_s(v, \theta_s) d\theta_s$$

(3-29)

$$\bar{u}_s = \int_0^{u_0} u \gamma_s g_s(u, \gamma_s) d\gamma_s = \int_0^{\gamma_s} \bar{u}_s g_s(u, \gamma_s) d\gamma_s$$

(3-30)

The formation rate of component $s$ in section $k$ can be written in terms of the mean volumes of component $s$ as follows.

Formation rate

$$\frac{1}{2} \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(v_{k-1} < u + v < v_k) (\bar{u}_s + v_s) \beta(u, v)n(u, t)n(v, t) dudv$$

(3-31)

The above equation has a similar form as Eqn. (3-24) except that the total volume flux is now replaced by the volume flux of component $s$ into section $k$. 
When the particles of section $k$ coagulates with smaller section particles and produce particles larger than $v_k$ then there is a net removal of particles from section $k$. The volume removal rate of component $s$ from section $k$ is

$$\text{removal rate} = \int_{v_0}^{v_k} \int_{v_k}^{v_{k+1}} \delta(u + v > v_k) \beta(u, v)n(u, t)n(v, t)dudv$$

(3-32)

If the newly formed particle, however, falls in the range $[v_{k-1}, v_k]$ then the volume influx of component $s$ in section $k$ is,

$$\text{volume influx} = \int_{v_0}^{v_{k-1}} \int_{v_k}^{v_k} \delta(u + v < v_k) \beta(u, v)n(u, t)n(v, t)dudv$$

(3-33)

The particles can be removed from section $k$ due to intra-sectional collision if the resulting particle is larger than $v_k$.

The volume flux out of section $k$

$$= \frac{1}{2} \int_{v_{k-1}}^{v_k} \int_{v_{k-1}}^{v_k} \delta(u + v > v_k) (\overline{u} + \overline{v}) \beta(u, v)n(u, t)n(v, t)dudv$$

(3-34)

The section $k$ particles can also be removed due to collision with particles from higher sectional size class.
The volume removal rate of component $s$

$$
V_{T_s} = \int_{v_{k-1}}^{v_k} \int_{v_x}^{v_y} u, \beta(u, v)n(u,t)n(v,t)dudv
$$

The Kronecker delta $\delta$ is not required in the above expression since the particles of section $k$ will obviously be removed when they collide with larger section particles. There is also a possibility that the particle will remain in section $k$ when two section $k$ particles collide but, it will not be considered in the particle dynamics equation since it does not produce any particle volume change in section $k$.

Now, the net volume flux $\frac{dF_{k,s}}{dt}$ of component $s$ in section $k$ can be written by combining the addition and removal rate equations.

$$
\frac{dF_{k,s}}{dt} = \frac{1}{2} \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(v_{k-1} < u + v < v_k)(u, v) + \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(u + v < v_k)(u, v)n(u,t)n(v,t)dudv
$$

$$
+ \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(u + v > v_k)(u, v)n(u,t)n(v,t)dudv
$$

$$
- \int_{v_0}^{v_{k-1}} \int_{v_0}^{v_k} \delta(u + v > v_k)(u, v)n(u,t)n(v,t)dudv
$$

(3-36)
The above equation can be modified by rewriting the integrals ranging over more than one section by a sum of integrals over each section as follows.

$$\frac{dF_{k,t}}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{i-1} \int_{v_{i-1}}^{v_i} \int_{v_{j-1}}^{v_j} \delta(u + v < v_k)(u_\pm + v_\pm)\beta(u,v)n(u,t)n(v,t)dudv$$

$$+ \sum_{i=1}^{k-1} \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} \delta(u + v < v_k)v_\beta(u,v)n(u,t)n(v,t)dudv$$

$$- \sum_{i=1}^{k-1} \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} \delta(u + v > v_k)u_\beta(u,v)n(u,t)n(v,t)dudv$$

$$- \frac{1}{2} \int_{v_{k-1}}^{v_k} \int_{v_{k-1}}^{v_k} \delta(u + v > v_k)(u_\pm + v_\pm)\beta(u,v)n(u,t)n(v,t)dudv$$

$$- \sum_{i=k+1}^{k+n} \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} u_\beta(u,v)n(u,t)n(v,t)dudv$$

(3-37)
In order to obtain a closed set of particle dynamics equations, it is required to find a relationship between \( g_s(v, \theta_s) \) and \( n(v, t) \) to \( F_{k_s} \). Therefore, two more equations will be necessary to obtain a closed set of equations. The first approximation, inherent to sectional formulation is to assume constant size distribution within each section which will eliminate \( n(v, t) \). Therefore,

\[
F_k(t) = \int_{v_{k-1}}^{v_k} vn(v, t) dv \\
= \int_{v_{k-1}}^{v_k} f(v, t) dv = \overline{f_k}(v_k - v_{k-1})
\]  

(3-38)

A series of step functions can be obtained from the \( \overline{f_k}(t) \) versus \( v \) plot. The area under each step will be equal to \( F_k(t) \).

From Eqn. (3-38) it can be written for each section,

\[
\frac{F_k(t)}{v_k - v_{k-1}} = \overline{f_k}(t) = vn(v, t)
\]

or

\[
n(v, t) = \frac{F_k(t)}{v(v_k - v_{k-1})}
\]  

(3-39)

In order to eliminate \( g_s(v, \theta_s) \), it is assumed that the mean volume fractions of all particles within a section is equal and independent of particle size inside the section i.e.,
If $g_s(v, \theta)$ does not depend on particle volume $v$ in section $k$. The volume of component $s$ in section $k$, 

$$F_{k,s} = \int_{v_{k-1}}^{v_k} \int_0^1 v \theta_s g_s(v, \theta) n(v, t) d\theta dv$$  \hspace{1cm} (3-40)$$

Using the above approximation into Eqn. (3-40), 

$$F_{k,s} = \int_{v_{k-1}}^{v_k} vn(v, t) dv \int_0^1 \theta_s g_s(v, \theta) d\theta$$

$$= \int_{v_{k-1}}^{v_k} vn(v, t) dv \frac{\bar{v}_s}{\bar{v}}$$  \hspace{1cm} (3-41)$$

$$= F_k \frac{\bar{v}_s}{\bar{v}}$$

or,

$$\frac{\bar{v}_s}{\bar{v}} = \frac{v F_{k,s}}{F_k}$$  \hspace{1cm} (3-42)$$

Now, the addition and removal rates of component $s$ for section $k$ can be expressed in terms of $\bar{v}_s$ and $F_{k,s}$ instead of $g_s(v, \theta)$. The final form of the multi-component sectional equation is as follows:
\[
\frac{dF_{k,s}}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \int_{v_{i-1}}^{v_i} \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < u + v < v_k) u F_{j,s} F_j \beta(u,v) \frac{F_i}{u(v_j - v_{j-1}) v(v_i - v_{i-1})} dudv
\]

\[
+ \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \int_{v_{i-1}}^{v_i} \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < u + v < v_k) v F_{j,s} F_j \beta(u,v) \frac{F_i}{u(v_j - v_{j-1}) v(v_i - v_{i-1})} dudv
\]

\[
+ \sum_{i=1}^{k-1} \int_{v_{i-1}}^{v_i} \delta(u + v < v_k) v F_{i,s} F_i \beta(u,v) \frac{F_k}{u(v_k - v_{k-1}) v(v_i - v_{i-1})} dudv
\]

\[
- \sum_{i=1}^{k-1} \int_{v_{i-1}}^{v_i} \delta(u + v > v_k) u F_{k,s} F_k \beta(u,v) \frac{F_i}{u(v_k - v_{k-1}) v(v_i - v_{i-1})} dudv
\]

\[
- \frac{1}{2} \sum_{i=1}^{k-1} \int_{v_{i-1}}^{v_i} \delta(u + v > v_k)(u + v) F_{k,s} F_k \beta(u,v) \frac{F_i}{u(v_k - v_{k-1}) v(v_i - v_{i-1})} dudv
\]

\[
- \sum_{i=k+1}^{k_{max}} \int_{v_{i-1}}^{v_i} u F_{i,s} F_i \beta(u,v) \frac{F_k}{u(v_k - v_{k-1}) v(v_i - v_{i-1})} dudv
\]

or,

\[
\frac{dF_{k,s}}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \left( u \beta_{i,j,k} F_i F_{j,s} + v \beta_{i,j,k} F_{j,s} F_i \right) \frac{1}{2} \sum_{i=1}^{k_{max}} \sum_{i=k+1}^{k_{max}} \beta_{i,k} F_i F_{k,s} - F_{k,s} \sum_{i=1}^{k_{max}} \beta_{i,k} F_i
\]

\[
- \frac{1}{2} \beta_{k} F_{k,s} F_{k,s} - F_{k,s} \sum_{i=k+1}^{k_{max}} \beta_{i,k} F_i
\]
where, the coagulation coefficients are defined as follows.

$$^1a \beta_{i,j,k} = \int_{v_{i-1}}^{v_i} \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < u + v < v_k) \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_j - v_{j-1})} dudv$$ (3-45)

$$^1b \beta_{i,j,k} = \int_{v_{i-1}}^{v_i} \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < u + v < v_k) \frac{v \beta(u,v)}{uv(v_i - v_{i-1})(v_j - v_{j-1})} dudv$$ (3-46)

$$^2 \beta_{i,k} = \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} \delta(u + v > v_k) \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} dudv$$ (3-47)

$$^3 \beta_{k} = \int_{v_{k-1}}^{v_k} \int_{v_{k-1}}^{v_k} \delta(u + v > v_k) \frac{(u + v) \beta(u,v)}{uv(v_k - v_{k-1})^2} dudv$$ (3-48)

$$^4 \beta_{i,k} = \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} dudv$$ (3-49)

$$^5 \beta_{i,k} = \int_{v_{i-1}}^{v_i} \int_{v_{k-1}}^{v_k} \delta(u + v < v_k) \frac{v \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} dudv$$ (3-50)

### 3.3.3 Discrete-Sectional Model

The discrete-sectional approach combines both the discrete and sectional size classes. It includes the interaction between discrete and sectional particles besides intra-discrete and intra-sectional coagulation. The discrete-sectional approach combines the features of
both discrete and sectional methods - accurate tracking of small molecular clusters by the
discrete formulation and computational advantages in tracking large particle size domain
by the sectional approach.

For the two component model, there will be two discrete regimes, one for each of the
components. Inter-component interaction in the discrete regime will not be allowed to
keep the system consistent with the actual process in consideration where the components
are formed at different times. The maximum number of discrete size classes are $i_{\text{max}}$ and
for both components namely iron and sulfur. The maximum number of sections and
components are $k_{\text{max}}$ and $s_{\text{max}}$ respectively.

The discrete representation in the discrete-sectional approach will include another
term for the removal of particles from a discrete class due to collision with any sectional
particle which is given by:

\[
\text{removal rate} = \int_{v_0}^{v_{\text{max}}} \beta(u,v) vn(u,t)n(v,t) du
\]

\[
= \sum_{k=1}^{k_{\text{max}}} \int_{v_{k-1}}^{v_k} \beta(u,v)(iv_{1,s}) \frac{f_{i,s}}{(iv_{1,s})} \frac{F_k}{u(v_k - v_{k-1})} du
\]

\[
= f_{i,s} \sum_{k=1}^{k_{\text{max}}} \beta_{i,k,s}^D F_k
\]
where,

$$4 \rho_{i,k,s}^D = \int_{v_{i-1}}^{v_i} \frac{(iv_{i,s})}{(iv_{i,s})} \frac{\beta(u,v)}{u(v_k - v_{k-1})} \, du$$  \hspace{1cm} (3-52)

Combining Eqn. (3-50) with Eqns. (3-18) and (3-19) the discrete representation becomes,

$$\frac{df_{i,s}}{dt} = G_i - f_{i,s} \sum_{j=1}^{i_{\text{max}}} 2 \beta_{i,j,s} f_{j,s} - f_{i,s} \sum_{s=1}^{k_{\text{max}}} 4 \rho_{i,k,s}^D F_k$$  \hspace{1cm} (3-53)

$$\frac{df_{i,s}}{dt} = \frac{1}{2} \sum_{j=1}^{i_{\text{max}}} 2 \beta_{j,i,s} f_{j,s} f_{i,s} - f_{i,s} \sum_{j=1}^{i_{\text{max}}} 2 \beta_{i,j,s} f_{j,s} - f_{i,s} \sum_{k=1}^{k_{\text{max}}} 4 \beta_{i,k,s} F_k$$  \hspace{1cm} (3-54)

Now the sectional regime equation also needs to be modified to include the following.

1. rate of formation of component $s$ in section $k$ due to the coagulation of two discrete particles from discrete size classes $i$ and $j$.

\[
\text{formation rate} = \frac{1}{2} \sum_{i=1}^{i_{\text{max}}} \sum_{j=1}^{i_{\text{max}}} \delta(v_{i,s} < v_{i,s} (i + j) < v_j (u + v)) \beta(u,v) n(u,t) n(v,t) \\
= \frac{1}{2} \sum_{i=1}^{i_{\text{max}}} \sum_{j=1}^{i_{\text{max}}} \delta(v_{i,s} < v_{i,s} (i + j) < v_j) v_{i,s} (i + j) \beta(iv_{i,s}, jv_{i,s}) \frac{f_{i,s}}{iv_{i,s}} \frac{f_{j,s}}{jv_{i,s}} \\
= \frac{1}{2} \sum_{i=1}^{i_{\text{max}}} \sum_{j=1}^{i_{\text{max}}} \beta_{i,j,k,s} f_{i,s} f_{j,s} \\
\]  \hspace{1cm} (3-55)
where, the coagulation coefficient

\[ \beta_{r,i,j,k,s}^{DDS} = \delta(v_{k-1} < v_{1,s}(i+j) < v_k) \frac{v_{1,s}(i+j) \beta(iv_{1,s}, jv_{1,s})}{(iv_{1,s})(jv_{1,s})} \]  

(3-56)

2. rate of formation of component \( s \) in section \( k \) due to the coagulation of discrete particles from discrete size class \( i \) and smaller sectional particles.

formation rate \[ = \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \int_{v_{j-1}}^{v} \delta(v_{k-1} < iv_{1,s} + u < v_k) \beta(u, iv_{1,s}) \frac{f_{i,r}}{u(v_j - v_{j-1})} du \]

\[ = \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \int_{v_{j-1}}^{v} \delta(v_{k-1} < iv_{1,s} + u < v_k) \beta(u, iv_{1,s}) \frac{f_{i,r}}{u(v_j - v_{j-1})} du \]

\[ + \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \int_{v_{j-1}}^{v} \delta(v_{k-1} < iv_{1,s} + u < v_k) \beta(u, iv_{1,s}) \frac{f_{i,r}}{u(v_j - v_{j-1})} du \]

\[ = \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \int_{v_{j-1}}^{v} \delta(v_{k-1} < iv_{1,s} + u < v_k) \beta(u, iv_{1,s}) \frac{f_{i,r}}{u(v_j - v_{j-1})} du \]

\[ + \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \int_{v_{j-1}}^{v} \delta(v_{k-1} < iv_{1,s} + u < v_k) \beta(u, iv_{1,s}) \frac{uF_{i,r}}{F_j} \] 

\[ = \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \beta_{r,i,j,k,s}^{D} f_{i,r} F_j \]

\[ + \sum_{r=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{k-1} \beta_{r,i,j,k,s}^{D} f_{i,r} F_j \]

(3-57)
where the coagulation coefficients are,

\[
\beta_{i,j,k,r}^D = \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < iv_{1,r} + u < v_k) \frac{\beta(u, iv_{1,r})}{(iv_{1,r})u(v_j - v_{j-1})} du
\]  

(3-58)

\[
\beta_{i,j,k,r}^D = \int_{v_{j-1}}^{v_j} \delta(v_{k-1} < iv_{1,r} + u < v_k) \frac{\beta(u, iv_{1,r})}{(iv_{1,r})u(v_j - v_{j-1})} du
\]  

(3-59)

3. rate of arrival of component \( s \) in section \( k \) when a discrete size particle collides with a section \( k \) particle and the coagulated particle stays in section \( k \).

\[
\text{formation rate} = \sum_{i=1}^{\infty} \sum_{r=1}^{V_i} \delta(v_{k-1} < iv_{1,s} + u < v_k)(v)\beta(u,v).n(u,t)n(v,t)du
\]

\[
= \sum_{i=1}^{\infty} \sum_{r=1}^{V_i} \delta(v_{k-1} < iv_{1,s} + u < v_k)(iv_{1,s})\beta(u, iv_{1,s}) \cdot \frac{f_{s,s}}{iv_{1,s}} \frac{F_k}{u(v_k - v_{k-1})} du
\]

\[
= F_i \sum_{i=1}^{\infty} s^\beta_{i,k,s} f_{s,s}
\]  

(3-60)

where,

\[
\beta_{i,k,s}^D = \int_{v_{k-1}}^{v_k} \delta(v_{k-1} < iv_{1,s} + u < v_k) \frac{(iv_{1,s}) \beta(u, iv_{1,s})}{(iv_{1,s})u(v_k - v_{k-1})} du
\]  

(3-61)

\[D_{i,m} \text{ and } S_k \text{ form } S_k\]
4. rate of removal of component $s$ from section $k$ when a discrete size particle and section $k$ particle form a particle larger than $v_k$.

\[
\text{removal rate} = \sum_{i=1}^{i_{\text{max}}} \int_{v_{i-1}}^{v_i} \delta(iv_{i,s} + u > v_k)(u)\beta(u,v)n(u,t)n(v,t)du
\]

\[
= \sum_{i=1}^{i_{\text{max}}} \int_{v_{i-1}}^{v_i} \delta(iv_{i,s} + u > v_k) \frac{uF_{k,s}}{F_k} \beta(u,iv_{i,s}) \frac{f_{i,s}}{iv_{i,s}} \frac{F_i}{u(v_k - v_{k-1})} du
\]

\[
= F_{i,s} \sum_{i=1}^{i_{\text{max}}} 2\beta_{i,k,s}^{0} f_{i,s}
\]  
(3-62)

where,

\[
2\beta_{i,k,s}^{0} = \int_{v_{i-1}}^{v_i} \delta(iv_{1,s} + u > v_k) \frac{u}{(iv_{1,s})} \frac{\beta(u,iv_{1,s})}{u(v_k - v_{k-1})} du
\]  
(3-63)

Combining the above equations (Eqns. 3-55 to 3-62) and Eqn. (3-44) the discrete-sectional equations for the first section can be written as:

\[
\frac{dF_{1,s}}{dt} = \frac{1}{2} \sum_{i=1}^{i_{\text{max}}} \sum_{j=1}^{j_{\text{max}}} \beta_{i,j,s}^{\text{DS}} f_{i,s} f_{j,s} + F_{1} \sum_{i=1}^{i_{\text{max}}} 5\beta_{1,k,s}^{0} f_{i,s} - F_{1,k} \sum_{i=1}^{i_{\text{max}}} 2\beta_{1,k,s}^{0} f_{i,s}
\]

\[- \frac{1}{2} \beta_{k} F_{1,s} f_{1,s} - F_{1,k} \sum_{i=2}^{i_{\text{max}}} 4\beta_{i,1} f_{i}
\]  
(3-64)
The discrete-sectional equations for section \( k \ (k \geq 2) \) is given as:

\[
\frac{dF_{i,s}}{dt} = \frac{1}{2} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \beta_{i,j,k,s} D D S f_{i,s} f_{j,s} + \frac{1}{2} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \left( \beta_{i,j,k} F_{i,s} F_{j,s} + \beta_{i,j,k} F_{i,s} F_{j,s} \right) + F_k \sum_{i=1}^{\text{max}} \beta_{i,k} F_{i,s}
\]

\[
+ \sum_{r=1}^{\text{max}} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \beta_{i,j,k,r} f_{i,s} F_{j,s} + \sum_{r=1}^{\text{max}} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \beta_{i,j,k,r} f_{i,s} F_{j,s} + F_i \sum_{r=1}^{\text{max}} \beta_{i,k,r} f_{i,s} F_{j,s}
\]

\[
- F_{k,s} \sum_{i=1}^{\text{max}} 2 \beta_{i,k,s} f_{i,s} - F_{k,s} \sum_{i=1}^{\text{max}} 2 \beta_{i,k} F_i - \frac{1}{2} F_k F_{k,s} F_{i,s} - F_{k,s} \sum_{j=1}^{\text{max}} 4 \beta_{i,k} F_i
\]  

(3-65)

The discrete-sectional equations (Table 3-1), collision frequency functions (Table 3-2) are given at the end of this chapter.

### 3.4 Growth of Carbon Fibers

A preliminary study of the carbon fiber growth has been made to examine the formation of fibers in the reactor. The fiber growth is calculated as follows. The diameter of the catalyst particle is a good approximation of the diameter of the filament that is initially produced by the catalyst. The number concentration of the catalyst particles determine the availability of carbon per fiber, which then limits the mass of carbon available to each catalyst particle for fiber growth. A brief description of the analysis of fiber growth is given below.

Methane gas is pyrolyzed in the reactor, and the carbon is deposited on the catalyst particles. The pyrolysis can be modeled by decomposition reactions (Bammidipati et al.,
1996) with different depositing species. Following is the simplest model where the acetylene is the depositing species i.e. carbon deposition on the catalyst particle is from acetylene.

\[ CH_4 \leftrightarrow 0.5C_2H_2 + 1.5H_2 \]  \hspace{1cm} (3-66)

\[ C_2H_2 + 2S \rightarrow 2C.S + H_2 \]  \hspace{1cm} (3-67)

In the above equations, \( S \) refers to the catalyst particle surface on which carbon deposition takes place and fiber is formed. It is assumed that acetylene is the depositing species.

The kinetics of fiber growth on catalyst particles is not available in the current literature. There is also not enough experimental data to determine the reaction rate constants for the fiber growth kinetics. Therefore, the reaction rate constants will be determined by simple trial and error method to match the calculated results with the set of experimental data. It is obvious that the reaction rate constants may not be highly accurate.

The net formation rates of the chemical species (based on the reaction mechanisms given by Eqns. (3-66) and (3-67) and the fiber thickening and lengthening rates are given below.
The rate of carbon depositing on the catalyst particles (on half of its surface area) and on the lateral surfaces of fibers is:

\[
\text{Total carbon deposition rate} = 2C_{C_2H_2} \cdot K_s \cdot (N \times 0.5 \times \text{surface area of the catalyst particle})
\]
\[
+ 2C_{C_2H_2} \cdot K' \cdot (N \times \text{lateral surface area of the fiber})
\]
\[
= 2C_{C_2H_2} \cdot K_s \cdot (N \times 0.5 \times \pi D_f^2) + 2C_{C_2H_2} \cdot K' \cdot (N \times \pi DL)
\]

(3-68)

In the above equation \(N\) is the number concentration of catalyst particles per unit volume of gas in the reactor, \(C_{C_2H_2}\) is the molar concentration of acetylene, \(K_s\) and \(K'\) are the surface reaction rate constants on the catalyst particle and the fiber respectively, \(D_f\) is the filament diameter which is taken to be the same as the catalyst particle diameter, \(D\) is the fiber diameter, and \(L\) is the fiber length.

The net rate of methane formation is given in terms of the species concentrations as:

\[
\frac{dC_{CH_4}}{dt} = -K_f \left( C_{CH_4} - \frac{C_{C_2H_2}^{0.5} \cdot C_{H_2}^{1.5}}{K_{eq}} \right)
\]

(3-69)

where, \(K_f\) and \(K_{eq}\) are concentration based forward reaction rate constant and equilibrium reaction rate constant for Eqn. (3-66). Data on fiber growth rates are obtained from data fit of General Motors Research Center results.

The net formation rates of acetylene and hydrogen gases are given by the following equations.
The fiber lengthening and thickening calculations are carried out by conserving the carbon deposited on the catalyst particle and the fiber.

3.4.1 Fiber Lengthening

The conservation equations for fiber lengthening are

\[
\frac{d}{dt} C_{C_2H_2} = 0.5K_f \left( C_{CH_4} - \frac{C_{C_2H_2}^{0.5} C_{H_2}^{1.5}}{K_{eq}} \right) - C_{C_2H_2} \cdot k_1 \cdot (N\pi \times 0.5 \times D_f^2) - C_{C_2H_2} \cdot k_2 \cdot (N \times \pi D_L)
\]

\[
(3-70)
\]

\[
\frac{d}{dt} C_{H_2} = 1.5K_f \left( C_{CH_4} - \frac{C_{C_2H_2}^{0.5} C_{H_2}^{1.5}}{K_{eq}} \right) + C_{C_2H_2} \cdot k_2 \cdot (N\pi \times 0.5 \times D_f^2) + C_{C_2H_2} \cdot k_2 \cdot (N \times \pi D_L)
\]

\[
(3-71)
\]

The fiber lengthening and thickening calculations are carried out by conserving the carbon deposited on the catalyst particle and the fiber.

3.4.1 Fiber Lengthening

The conservation equations for fiber lengthening are

\[
12 \times \text{carbon deposition rate on the catalyst} = \text{mass rate of carbon into the fiber filament}
\]

\[
= N \frac{d}{dt} (\rho \pi D_f L \xi)
\]

\[
= N \rho \pi D_f \xi \frac{dL}{dt}
\]

\[
(3-72)
\]
where, $\zeta$ is the wall thickness of the hollow filament (which is experimentally found to be equal to one-tenth of the catalyst particle diameter) and $\rho$ is the density of the deposited carbon. Again

\[
\text{carbon deposition rate on the catalyst} = 2K_C C_{\text{CH}_2} \left( N \times 0.5\pi \times D_f^2 \right) \tag{3-73}
\]

Substituting Eqn. (3-73) into Eqn. (3-72) the fiber lengthening rate can be obtained as:

\[
\frac{dL}{dt} = \frac{12K_C C_{\text{CH}_2} D_f}{\rho \zeta} \tag{3-74}
\]

### 3.4.2 Fiber Thickening

The conservation equations for fiber thickening are:

\[
12 \times \text{carbon deposition rate on the fiber} = \text{mass of carbon going in the fiber}
\]

\[
= N \frac{d}{dt} \left( \frac{\pi}{4} (D^2 - D_o^2) L \rho \right) = N\rho \frac{\pi}{4} \left( 2D \frac{dD}{dt} L + (D^2 - D_o^2) \frac{dL}{dt} \right) \tag{3-75}
\]

where, $D_o$ is the diameter of the hollow tube inside the filament.
Again,  

\begin{equation}
\text{carbon deposition rate on the fiber} = 2K_pC_{C,H_2}(N\pi DL) \tag{3-76}
\end{equation}

Using Eqn. (3-76) into Eqn. (3-75) the following rate for fiber thickening is obtained.

\begin{equation}
\frac{dD}{dt} = 48 \times K_p C_{C,H_2} \rho - \frac{(D^2 - D_0^2)}{2DL} \frac{dL}{dt} \tag{3-77}
\end{equation}

The reaction rate constants for fiber lengthening and thickening are based on experimental data on fibers produced in the GM reactor as provided by Tibbetts et al., (1992).

\begin{equation}
K_f = 10^{19.977T-0.558} e^{-52.782/T} \tag{3-78}
\end{equation}

and

\begin{equation}
K_{eq} = 10^{20.64T-4.03} e^{-29.990/T} \tag{3-79}
\end{equation}

The surface reaction rate constants are:

\begin{equation}
K_s = 9.8 \times 10^{-5} \sqrt{\frac{RT}{2\pi M}} \tag{3-80}
\end{equation}
and

\[ K_s^{-} = 1.75 \times 10^{-6} \sqrt{\frac{RT}{2\pi M}} \]  

(3-81)

In Eqns. (3-80) and (3-81), \( R \) is the universal gas constant and \( M \) is the molecular weight of the species (acetylene) that deposits carbon on the catalyst surface.
TABLE 3-1

Volume Conservation Equations for Particles in the Discrete-Sectional Model

\[ \frac{df_{i,s}}{dt} = G_s - f_{i,s} \sum_{j=1}^{\text{max}} \beta^D_{i,j,s} f_{j,s} - f_{i,s} \sum_{k=1}^{\text{max}} \beta^D_{i,k,s} F_k \]

First discrete size

\[ \frac{df_{i,s}}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta^DD_{j,s,j-i,s} f_{j,s} f_{i-j,s} - f_{i,s} \sum_{j=1}^{\text{max}} \beta^DD_{i,j,s} f_{j,s} - f_{i,s} \sum_{k=1}^{\text{max}} \beta^D_{i,k,s} F_k \]

Other discrete sizes

\[ \frac{dF_{1,s}}{dt} = \frac{1}{2} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \beta^{DDS}_{i,j,s} f_{i,s} f_{j,s} + F_i \sum_{j=1}^{\text{max}} \beta^D_{i,j,s} f_{j,s} - F_{i,s} \sum_{k=1}^{\text{max}} \beta^D_{i,k,s} f_{i,s} - \frac{1}{2} \beta_k F_{1,s} - F_{1,s} \sum_{i=2}^{\text{max}} \beta_{i,1,s} F_i \]

First section

\[ \frac{dF_{k,s}}{dt} = \frac{1}{2} \sum_{i=1}^{\text{max}} \sum_{j=1}^{\text{max}} \beta^{DDS}_{i,j,k,s} f_{i,s} f_{j,s} + \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \left( \beta_{i,j,k} F_{i,s} F_{j,s} + \beta_{i,j,k} F_{i,s} F_j \right) + F_k \sum_{i=1}^{k-1} \beta_{i,k} F_{i,s} + \sum_{r=1}^{i-1} \sum_{j=1}^{k-1} \beta^D_{r,j,k,s} f_{r,s} f_{j,s} + F_i \sum_{j=1}^{\text{max}} \beta^D_{i,k,s} f_{i,s} - F_{k,s} \sum_{i=1}^{\text{max}} \beta_{i,k,s} F_i - \frac{1}{2} \beta_k F_{k,s} - F_{k,s} \sum_{i=k+1}^{\text{max}} \beta_{i,k} F_i \]

Other sections
TABLE 3-2(a)
Coagulation Coefficient (Volume Based)
for Discrete-Sectional Model

Particles in two Discrete size classes colliding to form a new particle

\[ 1^D\beta_{i,j,i,s} = \beta(i_{v_{i,s}}, j_{v_{i,s}}) \frac{v_{i,s}(i + j)}{(i_{v_{i,s}})(j_{v_{i,s}})} \]

Particles in Discrete size class colliding with particles in a Sectional size class

\[ 1^s\beta_{i,k,i,s} = \int_{v_{j-1}}^{v_i} \delta(v_{k-1} < i_{v_{i,s}} + u < v_k)(i_{v_{i,s}})\beta(u,i_{v_{i,s}}) \frac{u}{(i_{v_{i,s}})u(v_j - v_{j-1})} \]

\[ 2^s\beta_{i,k,i,s} = \int_{v_{j-1}}^{v_i} \delta(v_{k-1} < i_{v_{i,s}} + u < v_k)(i_{v_{i,s}})\beta(u,i_{v_{i,s}}) \frac{u}{(i_{v_{i,s}})u(v_j - v_{j-1})} \]

\[ 3^s\beta_{i,k,i,s} = \int_{v_{k-1}}^{v_i} \delta(v_{k} < i_{v_{i,s}} + u < v_k)(i_{v_{i,s}})\beta(u,i_{v_{i,s}}) \frac{u}{(i_{v_{i,s}})u(v_k - v_{k-1})} \]

\[ 4^s\beta_{i,k,i,s} = \int_{v_{k-1}}^{v_i} \delta(v_{k} < i_{v_{i,s}} + u < v_k)(i_{v_{i,s}})\beta(u,i_{v_{i,s}}) \frac{u}{(i_{v_{i,s}})u(v_k - v_{k-1})} \]
TABLE 3-2(b)
Coagulation Coefficient (Volume Based)
for Discrete-Sectional Model

Particles in two Sectional size classes colliding to form a new particles in another size class

\[ ^{1a} \beta_{i,j,k} = \int_{v_{i-1},v_{j-1}}^{v_i,v_j} \delta(v_{k-1} < u + v < v_k) \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_j - v_{j-1})} \frac{dudv}{du} \]

\[ F_i \text{ and } F_j, s \text{ form } F_k,s \]

\[ F_{k,s} \]

\[ ^{1b} \beta_{i,j,k} = \int_{v_{i-1},v_{j-1}}^{v_i,v_j} \delta(v_{k-1} < u + v < v_k) \frac{v \beta(u,v)}{uv(v_i - v_{i-1})(v_j - v_{j-1})} \frac{dudv}{dv} \]

\[ F_i,s \text{ and } F_j \text{ form } F_k,s \]

\[ ^{2} \beta_{i,k} = \int_{v_{i-1},v_{k-1}}^{v_i,v_k} \delta(u + v > v_k) \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} \frac{dudv}{du} \]

\[ F_i \text{ and } F_k \text{ remove } F_k,s \text{ (i<k)} \]

\[ ^{3} \beta_{k} = \int_{v_{k-1},v_{k-1}}^{v_k,v_k} \delta(u + v > v_k) \frac{(u + v) \beta(u,v)}{uv(v_k - v_{k-1})^2} \frac{dudv}{dv} \]

\[ F_k \text{ and } F_k \text{ remove } F_k,s \]

\[ ^{4} \beta_{i,k} = \int_{v_{i-1},v_{k-1}}^{v_i,v_k} \frac{u \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} \frac{dudv}{du} \]

\[ F_i \text{ and } F_k \text{ remove } F_k,s \text{ (i>k)} \]

\[ ^{5} \beta_{i,k} = \int_{v_{i-1},v_{k-1}}^{v_i,v_k} \delta(u + v < v_k) \frac{v \beta(u,v)}{uv(v_i - v_{i-1})(v_k - v_{k-1})} \frac{dudv}{dv} \]

\[ F_i \text{ and } F_k \text{ form } F_k,s \text{ (i<k)} \]

where

\[
\beta(u,v) = \sqrt{\frac{6k_BT_{n,m}}{\rho_{p,m}}} \left[ \frac{1}{i} + \frac{1}{j} \right] \times (i^{1/3} + j^{1/3})^2 \]

Collision frequency function
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CFD Simulation Results

The flow and the temperature fields in the Pyrograf reactor have been calculated by using a 2-D approximation and neglecting the natural convection effects. It is expected that natural convection will be important in a scaled up reactor because the nondimensional parameter $G$ is larger than unity. A complete analysis of the scaled up reactor flow including the natural convection effect would require a complex 3-D analysis. Since the major focus of this study is on the catalyst formation, a simpler 2-D flow analysis was used.

The main focus of this study is the VGCF reactor at the General Motors research center which will be referred to as GM reactor in the following. The experimental studies on the catalyst particles and the carbon fibers could be made only on the GM reactor. Therefore, the GM reactor has been chosen for theoretical modeling and experimental studies. The theoretical results from the particle dynamics model of catalyst formation and growth are compared with the measured data from the GM reactor. The experimental data on fiber growth in the GM reactor has been used to obtain fiber growth kinetics. The temperature fields obtained from the CFD simulations have
been used in the subsequent particle growth and the fiber growth models. Finite elements CFD simulations have been carried out for the scaled up reactors and the results are given in Appendix A. The scaled up reactors have been simulated to study the feasibility of developing a production scale reactor with higher throughput. There was no experimental investigation made on the scaled up reactors and hence only the calculated temperature profiles are presented. The GM and the scaled up reactors have been modeled as 2-D axisymmetric models. The flow has been treated as a variable density flow due to the high temperature gradient along the flow. The variation of the physical and thermal properties of the fluid is significant in the reactor and hence the temperature dependent properties of the gas has been included in the simulation. The properties of methane has been used in the simulations since it comprises about 99 percent of the inlet gas.

The temperature distribution plot in the GM reactor is shown in Figure 4.1. The schematic diagram and the temperature boundary condition of the GM reactor is shown in Figure 2.4. The gas flow rate in the GM reactor is 2700 sccm and the furnace set point temperature is 1150°C. The gas temperatures inside the reactor have been plotted at three radial distances - near the centerline (at R=0.001 m), halfway between the centerline and the reactor wall (at R=0.004 m), and on the reactor wall (at R=0.00725 m). It is clear from Figure 4.1 that the temperature variation along the radial direction is negligible. Therefore, a 2-D analysis can be justified on the basis of the fact that the natural convection in this geometry would only result in greater temperature uniformity in the
radial direction by circulation and radial mixing. It will be assumed that the flow in the GM reactor is a simple plug flow, with no radial variation of flow velocity or temperature for the catalyst formation and fiber growth calculations.

Figure 4.1. Temperature distribution in the GM reactor with nominal gas flow rate of 2700 sccm. The set point temperature used is 1150°C. R is the radial distance from the center of the reactor.

Additional fluid flow and heat transfer simulations have been carried out to investigate the feasibility of scale-up for the reactor. The geometry and the temperature boundary condition of the scaled up reactor is shown in Figure 4.2. The scaled up reactor
has been simulated as a two dimensional axisymmetric model with temperature dependent gas properties (non-linear analysis). The results show a very complex flow even without natural convection effect as shown in Appendix-A.

![Temperature profile and reactor schematic](image)

**Figure 4.2.** Schematic diagram and temperature boundary condition of a scaled-up VGCF reactor.

### 4.2 Particle Nucleation and Growth Calculations

The particle dynamics equations were solved to simulate the process of catalyst nucleation in the VGCF reactor. Initially the particle growth simulations were carried out...
for one component particles (only iron) with iron pentacarbonyl in an inert carrier gas (helium) flow ranging from 2,700 sccm to 10,800 sccm at atmospheric pressure. These flow rates correspond to residence times of 0.25 to 1 second. The iron molecules are produced from iron pentacarbonyl decomposition inside the reactor at an elevated temperature. The temperature field was obtained from the temperature profile shown in Figure 4.1. The concentration of the iron pentacarbonyl in the inert carrier gas was varied from 2.1425E-5 mole/m$^3$ to 2.1425E-7 mole/m$^3$.

A total of 68 size classes were used in the calculations. There were 10 discrete size classes, and 58 sectional size classes. The last sectional size included particles of 1 micron size. Calculations of the particle size indicated that the largest particle is about 0.1 micron in diameter.

The thermal decomposition of iron pentacarbonyl and hydrogen sulfide takes place at different temperatures. The iron molecules are generated from iron pentacarbonyl at about 800°C (Tibbetts et al., 1993). The decomposition of hydrogen sulfide takes place in the temperature range of 600-860°C at atmospheric pressure (Kaloidas et al., 1989). It has been assumed that iron pentacarbonyl decomposition takes place instantaneously at 800°C when each iron pentacarbonyl molecule produces one iron molecule. The sulfur molecules are assumed to be produced at a constant rate in the temperature range of 600-860°C. The total decomposition of iron pentacarbonyl and hydrogen sulfide have been assumed.
Figure 4.3 shows the catalyst particle diameter as a function of inlet reactant concentration for different residence times in the reactor. The residence time for a flow rate of 2,700 sccm is 1 second. It can be observed that the catalyst particle diameter increases with increase in the reactant concentration and the residence time. These trends are to be expected since inter-particle collisions will continue to increase the particle size with increase in residence time. As the reactant concentration goes up, more iron molecules are produced and contribute to the growth of the catalyst particles by particle-particle collisions.

Figures 4.4, 4.5, and 4.6 show the development of the catalyst particle size distribution with time in the flow reactor. The catalyst particles range from 20 to 150 nm. A 20 nanometer particle is a sintered cluster composed of about 500,000 molecules. Starting with single molecules, the catalyst particles grow rapidly with time, and the average size increases to about 100 nanometers in about one second.
Figure 4.3. Size (average diameter) of catalyst particles (single component) for different iron pentacarbonyl concentrations and residence times.
Figure 4.4. Particle size distribution (single component) obtained from particle collision model for residence time = 0.25 second and iron pentacarbonyl concentration = $2.1425 \times 10^{-5}$ mole/m$^3$. 
Figure 4.5. Particle size distribution (single component) obtained from particle collision model for residence time = 0.5 second and iron pentacarbonyl concentration = $2.1425 \times 10^5$ mole/m$^3$. 
Figure 4.6. Particle size distribution (single component) obtained from particle collision model for residence time = 1.0 second and iron pentacarbonyl concentration = 2.1425x10^{-5} mole/m^3.

Experiments were also carried out in the VGCF reactor with an initial reactant concentration of 2.1425E-5 mole/m^3 of iron pentacarbonyl in helium at atmospheric
pressure for different residence times. The catalyst particles that were produced were then examined, and average sizes were determined. Figure 4.7 shows the comparison of the average catalyst particle size obtained from experiments with the average particle size from the analytical model. The catalyst particles in the experiment grow to about 100 nanometers for a residence time of about 1 second, after which there is very little growth of the catalyst particle. This indicates that, as the number of particles is reduced after a second of residence time, the inter-particle collisions become negligible since the collision frequency depends on the product of the concentrations of the colliding particles. The catalyst particles which are produced in the experimental VGCF reactor are not truly spherical; therefore the data points represent a characteristic size of the particles. It can be seen that the experimental results compare reasonably well with the simulation for different residence times, and the trends of the model results and experiment are very similar.
Figure 4.7. Catalyst particle diameter for different residence times with iron pentacarbonyl concentration = $2.1425 \times 10^{-5}$ mole/m$^3$. The diameter is obtained by averaging the particle distributions as shown in Figures 4.4, 4.5, and 4.6.

The experimental catalyst particle size distributions were determined by their number frequencies and then compared with analytical results for single component coagulation. The iron pentacarbonyl concentration in the carrier gas (helium) used is 4.30E-6 K mole/m$^3$. The residence times considered are 0.12, 0.20, 0.57, and 1.41 seconds and the particle number concentration versus particle diameter plots are shown in Figures 4.8,
4.9, 4.10, and 4.11 respectively. The particle size has a normal distribution with a mean that represents the maximum number concentration of the particles. The mean particle size increases with the increase in the residence time. The experimental and simulated results have similar trends and values which indicate that the particle dynamics model can predict the catalyst particle sizes in the reactor.

![Graph](image)

Figure 4.8. Number concentrations (single component) of different sized catalyst particles for a residence time of 0.12 second. The temperature in the reactor is 1150°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 Kmole/m³.

It has been found from experiments that the addition of sulfur in the iron catalyst particles increases the lengthening rate of vapor grown carbon fibers. The presence of
sulfur lowers the melting temperature of the catalyst particles. The carbon deposited on the molten catalyst can diffuse through the particle more favorably and thus produces a hollow slender filament. Consequently, carbon fibers produced with sulfur added to the catalyst particles have a higher aspect ratio and better qualities. The effectiveness of the catalyst particle depends on its optimum composition. Therefore, the multi-component

Figure 4.9. Number concentrations (single component) of different sized catalyst particles for a residence time of 0.20 second. The temperature in the reactor is 1150°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 K mole/m³.
particle coagulation model will be very useful in determining the reactor operating parameters and inlet gas compositions to obtain the desired catalyst composition. To investigate the catalyst particle growth inside the VGCF reactor, calculations have been carried out for the GM reactor in which only iron pentacarbonyl and hydrogen sulfide gas were used with the carrier gas (helium). The set point temperature used was 1158°C.

Figure 4.10. Number concentrations (single component) of different sized catalyst particles for a residence time of 0.57 second. The temperature in the reactor is 1150°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 K mole/m³.
The particle diameter is calculated for a fully sintered, spherical particle. This is a reasonable approximation since iron and sulfur mixtures are liquid at temperature of 880°C and above for a sulfur fraction of 52 percent in the catalyst particle. The calculated values of the atomic fraction of sulfur in the catalyst particles are shown in Figure 4.12 for the whole spectrum of catalyst sizes. The sulfur atomic fraction in the feedstock and iron pentacarbonyl

![Graph](image)

**Figure 4.11.** Number concentrations (single component) of different sized catalyst particles for a residence time of 1.41 seconds. The temperature in the reactor is 1150°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 K mole/m³.
concentration in the inlet gas are 0.2 and $4.3 \times 10^{-3}$ mole/m$^3$ respectively. Figure 4.12 shows that the atomic fraction of sulfur decreases for larger catalyst particles up to 40 nanometer size. Beyond this size the composition of the larger catalyst particles, do not vary significantly. The results from two sets of calculation using residence times of 0.12 and 1.41 seconds show similar trends in catalyst composition (Figure 4.12).

Figure 4.12. Sulfur atomic fraction in the catalyst particle (multi-component model) for different residence times. The temperature in the reactor is 1158°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 Kmole/m$^3$. Sulfur atomic fraction in the feedstock is 0.2.
The amount of hydrogen sulfide has been varied in the inlet gas to calculate the sulfur fraction (atomic) in the catalyst particles for different residence times. From each set of calculation a representative size of catalyst particle is chosen which has the highest number concentration. The set point temperature was kept at 1158°C, iron pentacarbonyl concentration in the inlet gas was 4.3x10^{-3} mole/m^3. The atomic fraction of sulfur used in the inlet gas are 0.2, 0.4, and 0.6. Figure 4.13 shows that the catalyst particles will have higher sulfur content for an inlet gas richer in hydrogen sulfide if the same residence time is used. The increase of sulfur content in the catalyst particle is much higher for the same amount of increment in consecutive increase of the feedstock sulfur fraction. The sulfur fraction in the catalyst particles are shown in Figure 4.14 as a function of sulfur fraction in the feedstock for residence times of 0.12, 0.2, 0.57 and 1.41 seconds. Set point temperature of 1158°C and iron pentacarbonyl concentration of 4.3x10^{-3} mole/m^3 have been used in the inlet gas. It can be noticed from Figure 4.14 that for a larger value of sulfur fraction in the feedstock the sulfur fraction in the representative catalyst particles reduces as the residence time is increased. The fraction of sulfur in the catalyst particles in the VGCF reactor can be controlled by adjusting the residence time for a given feedstock composition.
Figure 4.13. Sulfur atomic fraction in the catalyst particle (multi-component model) as a function of residence times. Different sulfur atomic fractions in the feedstock are used for the calculations. The temperature in the reactor is 1158°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 K mole/m³.
Figure 4.14. Sulfur atomic fraction in the catalyst particle (multi-component model) as a function of sulfur atomic fraction in the feedstock. Different residence times are used for the calculations. The temperature in the reactor is 1158°C. Iron pentacarbonyl concentration in the carrier gas (helium) at the inlet is 4.30E-6 K mole/m$^3$.

Experimental measurements of catalyst particle composition have been carried out with the GM reactor to validate the multi-component particle dynamics model. The inlet gas is composed of iron pentacarbonyl and hydrogen sulfide gas with concentrations of 0.0196 mole/m$^3$ and 0.0785 mole/m$^3$ respectively. Helium gas was bubbled through liquid iron pentacarbonyl at room temperature and its concentration was determined from
the pressure measurements. The feedstock was fed at room temperature and the set point temperature was 1176°C. The experimental and calculated values of iron fractions in the catalyst particles are shown in Figure 4.15 for different residence times. The calculated values of iron fraction in the catalyst particles agree reasonably well with the experimentally measured values.

The focus of this study is to examine the formation of catalyst particles in the flow. The results of the above study provides a basis for the calculation of fiber growth in the reactor. The diameter of the catalyst particle is a good approximation of the diameter of the fiber that is initially produced by the catalyst. The number concentration of the catalyst particles determine the availability of carbon per fiber; which then limits the mass of carbon available to each catalyst particle for fiber growth. Carbon fibers were grown in the GM reactor using a set point temperature of 1131°C, concentration of methane in the feedstock is 0.04 mole/m³. The concentration of iron pentacarbonyl and hydrogen sulfide in the feedstock were 4.3E-6 Kmole/m³ and 1.08E-6 Kmole/m³ with the residence time varying from 10 to 80 seconds.
Figure 4.15. Catalyst particle composition from experiment and calculations. The feedstock is composed of iron pentacarbonyl (0.0196 mole/m$^3$) and hydrogen sulfide (0.0785 mole/m$^3$). The temperature in the reactor is 1176°C.

4.3 Fiber Growth Simulation Results

Figures 4.16 and 4.17 show the diameter and length of the fiber as obtained from integration of the proposed kinetic model. As was mentioned earlier, the initial fiber
diameter was taken to be the same as the catalyst diameter for the simulation of fiber growth. The model simulations indicate a linear growth rate for both the diameter and length of the fiber.

![Graph showing fiber diameter vs. residence time](image)

**Figure 4.16.** Average fiber diameter from model results for different residence times with initial methane concentration = 0.03987 mole/m$^3$. 
Figure 4.17. Average fiber length (from theoretical calculations) at different residence times with initial methane concentration $= 0.03987 \text{ mole/m}^3$. 
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The synthesis of carbon fibers in the Pyrograf reactor was discovered at General Motors research facility approximately twenty years ago. Since then, the reactor and the product have been investigated by a number of researchers to analyze and model the processes involved in fiber synthesis. The investigations and models have been primarily based on experimental research, and empirical formula based on experiments.

There are three distinct phenomena that take place inside a Vapor Grown Carbon Fiber (VGCF) reactor. The phenomena are - gas flow and heat transfer, particle formation and growth, and the carbon fiber growth. Therefore, the theoretical study of a VGCF reactor requires CFD simulations, particle dynamics modeling, and CVD modeling to investigate the temperature and the flow field, catalyst particle formation and growth, and fiber growth processes.

The particle and the fiber growth kinetics are strongly temperature dependent. The size of the catalyst particle determines the diameter of the hollow filament of the fiber and consequently the diameter of the carbon fiber. The number concentration of the catalyst particle determines the number concentration of carbon fibers and hence the availability of carbon for deposition on the fiber during the fiber growth. The catalyst size and their number concentration will determine the size of the carbon fiber for a given
amount of carbon deposition. The percentage (atomic fraction) of sulfur in the catalyst particle determines its catalytic property.

Analysis of the process, including heat transfer and fluid flow, catalyst particle formation and growth, and fiber growth has been carried out in this study. The temperature field inside different VGCF reactors have been obtained by using a finite element commercial computational fluid dynamics software called FIDAP. From an axisymmetric modeling of the VGCF reactor it was observed that the temperature distribution inside the smaller reactor is almost invariant in the radial direction. Any circulation in the radial direction due to buoyancy-induced natural convection inside the reactor will yield a more uniform temperature along the radial direction. Therefore, this reactor was selected for the catalyst particle growth model. The radially uniform temperature field inside the reactor was the basis of assuming a plug flow for subsequent particle dynamics and fiber growth modeling.

The results from FIDAP are used as the temperature field in the reactor during the catalyst particle growth and the fiber growth modeling. The particle dynamics model provides the size distribution, concentration, and composition of the catalyst particles. Discrete-sectional approach has been used in modeling the particle growth dynamics, this technique is capable of tracking the smaller particles as well as the larger particles more accurately than a simpler sectional approach. The discrete-sectional model is computationally little less accurate than the purely discrete approach but is much less memory intensive and feasible. In this study the range of particle sizes is quite large and
is therefore a purely discrete modeling will be unrealistic. The catalyst particle growth model inside the reactor provides information regarding the sulfur content in the catalyst particle. It should be noted that the catalytic property of the particles is very sensitive to the fraction of sulfur in the particles. The desired catalytic effect will diminish with a slight excess or deficit of sulfur fraction than the optimum value.

The VGCF reactor has been simulated to predict the catalyst particle sizes in the range of 10-200 nanometer. The carbon fiber that grows from this catalyst will have a diameter in the size range of 50-500 nanometer. The experimental results are limited to certain catalyst size distribution and composition for different residence times and gas compositions. However, there appears to be reasonable agreement between the predicted and experimental values.

The carbon fiber growth model has been developed by using reaction kinetics from a limited set of experimental data, and could not be verified for different reactor input parameters. Further experimental and numerical investigations are recommended in order to determine a fiber growth kinetics that can be used to develop a comprehensive fiber growth model.
REFERENCES


APPENDIX - A

CFD SIMULATION RESULTS OF SCALED UP REACTOR

The temperature distribution inside the scaled up reactor is shown in Figure A.1 with methane flowrate of 19250 sccm, set point temperature of 1100°C. It can be seen from Figure A.1 that there is a large temperature difference in the radial direction. The gas

Figure A.1. Temperature distribution in the scaled-up reactor with methane gas flow rate of 19250 sccm. The set point temperature used is 1100°C. Inlet gas temperature is 25°C. R is the radial distance from the center of the reactor.
near the center of the reactor does not heat up sufficiently to react chemically and participate in the carbon fiber formation. Since the inlet of the reactor is small, the gas flows into the reactor as a core jet and the central part of the jet flows at a high velocity and can not get heated sufficiently. Increased thermal diffusion in the radial direction is required in order to increase the throughput by enhancing the chemical reactions. The effects of the following parameters on the temperature field have been studied.

1. Inlet gas temperature
2. Reactor set point temperature
3. Gas flow rate in the reactor, and
4. Size of the reactor inlet

The temperature of the discharge gas at the exit of the reactor is high enough to reheat the inlet gas if a heat exchanger is used and hence can save thermal energy input into the reactor. Three inlet gas temperatures have been used: 25°C, 200°C, and 400°C. Figure A.2 shows the temperature plots at the center of the reactor with different inlet gas temperatures for a set point temperature of 1100°C. The gas flow rate used is 19250 sccm. It can be observed from Figure A.2 that a higher temperature can be obtained at the center of the reactor with an inlet gas temperature higher than the room temperature.

The desired temperature distribution must be obtained inside the reactor to maximize the throughput. The reactor set point temperature is one of the operating parameters
which have been varied to study the temperature distribution. The set point temperatures used are 1050°C, 1150°C, and 1300°C. The temperature distribution inside the reactor with different set point temperatures are shown in Figures A.3 and A.4. The temperature near the reactor wall is shown in Figure A.3, and between the center and the wall is shown in Figure A.4. From both Figures A.3 and A.4, it can be observed that the gas temperature inside the reactor can be increased by increasing the energy input into the system. The energy input can not be increased without bound due to the fact that the gas must be cooled before it is exhausted from the system and also because of the reactor’s construction material constraints. The beneficial side effect of higher reactor temperature is a higher degree of graphitization in the carbon fibers which results in superior structural properties. The inlet gas was fed into the reactor at room temperature at a flow rate of 19250 sccm.
Figure A.2. Temperature distribution in the scaled-up reactor with different inlet gas temperatures. Methane gas flow rate is 19250 sccm. The set point temperature used is $1100^\circ C$.

Figure A.3. Gas temperatures near the reactor wall ($R=0.068$ m) in the scaled-up reactor with different set point temperatures. Methane gas flow rate is 19250 sccm. The inlet gas temperature is $25^\circ C$. 
Figure A.4. Gas temperatures between the center and the reactor wall (R=0.045 m) in the scaled-up reactor with different set point temperatures. Methane gas flow rate is 19250 sccm. The inlet gas temperature is 25°C.

Another way to increase the throughput is to increase the gas flowrate in the system. Three different gas flowrates; base flowrate (19250 sccm), double flowrate (38500 sccm), and quadrupled flowrate (77000 sccm) have been used to study the temperature distribution inside the scaled up reactor. The temperature of the inlet gas was 25°C in this set of simulations. The temperature distribution inside the reactor is shown in Figure A.5 for base flowrate, setpoint temperature of 1150°C. It can be noticed from Figure A.5 that the thermal entrance length is about the half of the reactor length. Figures A.6, A.7, and A.8 show the temperature distribution in the scaled up reactor with base, double and quadrupled flowrates near the center, middle of the center and reactor wall, and near the
Figure A.5. Temperature distribution in the scaled-up reactor with set point temperature of 1150°C. Methane gas flow rate is 19250 sccm. The inlet gas temperature is 25°C.
Figure A.6. Gas temperature near the center (R=0.01 m) in the scaled-up reactor with different gas flow rates. Reactor set point temperature is 1150°C. The inlet gas temperature is 25°C.
reactor wall respectively. The gas temperatures near the reactor wall is same for all the flowrates due to the fact that the gas is almost stationary near the wall. From Figures A.6 and A.7 it can be observed that the increased channeling effect due to higher gas flowrates diminishes away from the center of the reactor. The temperature distribution

**Figure A.7.** Gas temperature between the center and the wall (R=0.045 m) in the scaled-up reactor with different gas flow rates. Reactor set point temperature is 1150°C. The inlet gas temperature is 25°C.
with higher flowrates reveal that the gas can be heated sufficiently in the reactor to produce carbon fibers with flowrates as high as 38500 sccm. Setpoint temperature of 1300°C has been used with different flowrates; the gas temperatures near the wall is same for all cases as shown in Figure A.9.

![Figure A.8](image)

Figure A.8. Gas temperature near the wall (R=0.068 m) in the scaled-up reactor with different gas flow rates. Reactor set point temperature is 1150°C. The inlet gas temperature is 25°C.
Figure A.9. Gas temperature near the wall (R=0.068 m) in the scaled-up reactor with different gas flow rates. Reactor set point temperature is 1300°C. The inlet gas temperature is 25°C.

The jet-like channeling effect near the central part of the reactor can be reduced by increasing the inlet pipe diameter. Two flowrates, base flowrate and double flowrate, have been considered for two inlet pipe diameters (base diameter = 3/8 inch and expanded diameter=3.0 inches). The temperature plots in between the wall and the center of the reactor for the four possible cases are shown in Figure A.10 with set point temperature of 1150°C and gas inlet temperature of 25°C. The gas near the reactor inlet can diffuse more in the radial direction for a larger inlet pipe (with the same flowrate).
Figure A.10. Gas temperature between the center and the wall (R=0.045 m) in the scaled-up reactor with different gas flow rates and inlet diameter. Reactor set point temperature is 1150°C. The inlet gas temperature is 25°C.

BDBF=base inlet diameter and base flowrate
EDBF=expanded inlet diameter and base flowrate
BDDF=base inlet diameter and double flowrate
EDDF=expanded inlet diameter and double flowrate

Therefore, more thermal energy will be consumed near the reactor wall (because of higher flowrate near the wall) and there will be less heating of the central gas near the inlet as shown in Figure A.10.
Another set of CFD simulations have been carried out for the scaled up reactor to investigate the consequences of increasing the reactor tube diameter (also the inlet and outlet diameters such that the same ratio of the cross-sectional areas of the reactor and the inlet/outlet tubes remain unchanged) and gas flowrates. The heater length in this study is larger than the one used in the previous set of scaled up reactor. The objectives of this set of simulation are to investigate the temperature field and determine whether the reactor can be scaled-up further for higher throughput. In this study two reactor tube sizes have been studied - their diameters are 5.3 inches and 8.25 inches. In all of these cases the set point temperature and the inlet gas temperature were kept at 1150°C and 25°C respectively. The gas flowrates used are 58,840 sccm, 88,260 sccm, and 117,680 sccm. Figure A.11 shows the temperature distribution in the 5.3 inches reactor with a gas flowrate of 58,840 sccm and tube thermal conductivity of 4 W/(m-K). The temperature field looks very similar to the one shown in Figure A.1. The temperature distribution in the 8.25 inches reactor with tube thermal conductivity of 4 W/(m-K) are shown in Figures A.12, A.13, and A.14 for flowrates of 58,840 sccm, 88,260 sccm, and 117,680 sccm respectively. It can be observed from Figures A.12, A.13, and A.14 that the gas temperature reduces with the increase in the flowrate but the temperatures are in a range that can sustain the carbon fiber growth in all three cases. Figures A.15 through A.18 show the gas temperature at a given radius in the 8.25 inches reactor for different flowrates. For smaller gas flowrates the gas temperature near the center of the reactor is lower near the inlet which increases in the downstream side of the reactor. The thermal
conductivity of 4 W/(m-K) has been used for the reactor tube material. It is also evident from Figures A.15 - A.18 that the gas temperature for a smaller flowrate increases at a higher rate with the increase in the radial distance.

Figure A.11. Temperature distribution inside the scaled up base reactor (reactor tube diameter=5.3 inches, thermal conductivity of the tube material is 4.0 W/m-K) with base flowrate (flowrate=58,840 sccm).
Figure A.12. Temperature distribution inside the scaled-up reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) with base flowrate (flowrate=58,840 sccm).
Figure A.13. Temperature distribution inside the scaled-up reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) with flowrate of 88,260 sccm.
Figure A.14. Temperature distribution inside the scaled-up reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) with flowrate of 117,680 sccm.
Figure A. 15. Temperature distribution inside the scaled-up reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) at a radial distance of 0.03m for different flowrates.
Figure A.16. Temperature distribution inside the scaled-up reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) at a radial distance of 0.05m for different flowrates.
Figure A.17. Temperature distribution inside the scaled-up ASI reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) at a radial distance of 0.07m for different flowrates.
Figure A. 18. Temperature distribution inside the scaled-up ASI reactor (reactor tube diameter=8.25 inches, thermal conductivity of the tube material is 4.0 W/m-K) at a radial distance of 0.09m for different flowrates.