CHEMICAL VAPOR DEPOSITION/CHEMICAL VAPOR INFILTRATION
OF PYROCARBON IN POROUS CARBON

A Dissertation

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by

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Abstract

by

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A chemical vapor deposition/infiltration reactor used to manufacture carbon aircraft brakes has been simulated numerically. This simulation accounts for a homogeneous gas reaction mechanism as well as a heterogeneous surface reaction mechanism. Non-Boussinesq equations are used to predict fluid flow, heat transfer, and species concentrations inside the reactor and porous brakes. A time-splitting algorithm is used to overcome stiffness associated with the reactions. A commercial code is used to solve for the convection/diffusion step while an implicit time-integration algorithm is used to solve for the reaction step. Results showing the flow, temperature and concentration fields, as well as the deposition rate of carbon, are presented.

The direct solution of large scale coupled nonlinear differential algebraic equations (DAE) is extremely difficult if not impossible to obtain. Moreover, such solution is beyond the capability of present computers for unsteady and multidimensional problems that include, multi-species, gas phase as well as surface chemical reactions, and surface to surface radiation. Therefore, we propose an integration procedure that employs the projection (fractional-step) method for the solution of the momentum equation. This method is based on operator decomposition where the pressure is obtained by solving a Poisson equation followed by a
projection or correction step for the velocity field so that it satisfies the conservation of mass equation. In addition we use a symmetric Strang operator-splitting algorithm to overcome stiffness that arises from chemical reactions.
To the gentle spirit of my mother and grandmother, my father and sisters, and my in-laws in Egypt.

A special dedication to my wife and love Marian.
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SYMBOLS

Roman symbols

\( A_i \)  Surface area of element \( i \)
\( a_j \)  Kinetic rate constant of reaction \( j \)
\( Bo \)  Boltzmann number
\( C_{\infty}() \)  Active site on Carbon surface
\( C_{\infty}(i) \)  Occupied site on carbon surface by species \( i \)
\([C_k]\)  Gas concentration or surface concentration of species \( k \)
\( C_E \)  Ergun constant
\( Conv_i \)  Conversion of species \( i \)
\( c_p \)  Specific heat at constant pressure
\( c_{p_i} \)  Specific heat at constant pressure of species \( i \)
\( Da \)  Darcy number
\( D_{iM}^e \)  Effective mass diffusivity of species \( i \) in methane
\( D_{iM} \)  Binary mass diffusivity of species \( i \) in methane
\( D_{MM} \)  Binary mass diffusivity of methane in methane
\( D_i^k \)  Knudsen diffusivity of species \( i \)
\( e_i \)  Absolute tolerance for nodal point \( i \)
\( E_j \)  Activation energy of reaction \( j \)
\( E_j \)  Activation energy of reaction \( j \)
$F_{ij}$  View factor

$Dk$ Damköhler number

$\bar{F}$ Source matrix

$F$ Discrete source matrix

$Fr$ Froude number

$f_1, f_2, f_3$ Represent continuity, momentum, and energy equations

$G$ Irradiation elemental matrix

$G_i$ Irradiation of surface element $i$

$g$ Unit vector in the direction of gravity

$h_i$ Enthalpy per unit mass of species $i$

$h^0_{i,f}$ Standard enthalpy of formation per unit mass of species $i$

$I$ Identity Tensor

$I_i$ Inhibition function of species $i$

$J^m_j$ Barycentric diffusion mass flux of species $j$

$J$ Radiosity elemental matrix

$K$ Stiffness matrix

$K$ Discrete stiffness matrix

$k$ Thermal conductivity

$k_i$ Thermal conductivity of species $i$

$K_j$ Gas-phase or surface reaction rate constant of equation $j$

$L_p, L, R_{o1}, R_{o2}, R_{in}$ Reactor dimensional geometrical parameters

$l_p, l, r_{o1}, r_{o2}, r_i$ Reactor dimensionless geometrical parameters

$L_e, M_e, N_e$ Number of nodal points within each element

$M$ Multicomponent mean molecular mass

$\bar{M}$ Time-dependent matrix
$M_i$ Molecular mass of species $i$

$N$ Total number of species

$N_d$ Number of degrees of freedom

$N_g$ Number of gaseous species

$N_s$ Number of solid species

$N_r$ Number of chemical reactions

$n$ Surface normal unit vector

$P$ Column vector of element nodal point of unknown pressure

$Pe$ Peclet number

$p_i$ Partial pressure of species $i$

$p$ Thermodynamic pressure

$\bar{Q}$ Volumetric flow rate

$\bar{Q}_{i}^{in}$ Inlet volumetric flow rate of species $i$

$\bar{Q}_{i}^{out}$ Outlet Volumetric flow rate of species $i$

$Q_i$ Local error for nodal point $i$

$R_{o1}, R_{o2}$ Outlet reactor radii

$R$ Reactor radius

$r_{tot}$ Relative tolerance

$R_1, R_2, R_3$ Residuals

$Re$ Reynolds number

$\mathcal{R}$ Universal gas constant

$\dot{r}_i$ Production rate of species $i$ per unit volume of the gas-phase or per unit area of the surface

$r$ Radial coordinate

$\bar{r}_{ij}$ Distance between element surface $i$ and element surface $j$
$r_f$ Carbon fiber radius

$r_p$ Pore radius

$Sc$ Schmidt number

$Sel_i$ Selectivity of species $i$

$S_{ir}, S_{or}, L_d$ Substrate dimensional geometrical parameters

$S_v$ Ratio of substrate surface area/substrate volume

$t$ Time

$T$ Temperature

$\mathbf{T}$ Column vector of element nodal point of unknown temperature

$\mathbf{U}_i$ Column vector of element nodal point of unknown velocity

$\mathbf{U}_D$ Darcian gas velocity vector field

$\mathbf{u}_g$ Gas velocity vector field

$|\mathbf{u}_g|$ Magnitude of gas velocity

$\mathbf{u}_m$ Mean velocity in the axial direction

$\mathbf{u}_k^d$ Mass diffusion velocity of gaseous species $k$

$V$ Column solution vector of unknowns

$V_i$ Atomic molar diffusion volume of species $i$

$v$ Vertical velocity component

$W_f$ Fiber half-width

$\mathbf{x}$ Column coordinate vector

$Y_i$ Mass fraction of species $i$

$Yield_i$ Yield of species $i$

$z$ Axial coordinate

$Z_k(n)$ Site fraction of species $k$ of phase $n$
Greek symbols

\( \alpha \)  Thermal diffusivity
\( \beta \)  Volumetric thermal expansion coefficient
\( \beta_j \)  Temperature dependence exponent of reaction \( j \)
\( \Gamma_n \)  Site density of phase \( n \)
\( \Gamma_{tot} \)  Total site density
\( \gamma_i \)  Sticking coefficient of species \( i \)
\( \delta_{ij} \)  Interphase drag parameter
\( \Upsilon \)  Energy source term
\( \Upsilon_k \)  Energy source term associated with species \( k \)
\( \epsilon \)  Emissivity
\( \varepsilon_g \)  Gas volume fraction (porosity)
\( \varepsilon_{go} \)  Gas initial porosity
\( \eta^b, \eta^k, \eta^v \)  Bulk diffusion, Knudsen diffusion, and viscous transport tortuosity
\( \Theta, \Psi, \Phi \)  Column vectors of the interpolating (shape) functions
\( \theta_i, \psi_i, \phi_i \)  Interpolating (shape) functions at nodal point \( i \) within element
\( \kappa \)  Permeability of substrates
\( \lambda \)  Binary characteristic function
\( \mu \)  Gas dynamic viscosity
\( \mu_i \)  Gas dynamic viscosity of species \( i \)
\( \nu \)  Gas kinematic viscosity
\( \nu_{ij} \)  Reactant stoichiometric coefficient of species \( i \) in reaction \( j \)
\( \nu_{ij}'' \)  Product stoichiometric coefficient of species \( i \) in reaction \( j \)
\( \Xi \)  Reference production rate
\( \xi \)  Dimensionless temperature ratio \( 1 - \frac{T_{in}}{T_{wall}} \)
\(\xi_1, \xi_2, \xi_3\) Natural barycentric (or area) coordinates

\(\Pi\) Hydrodynamic/hydrostatic gas pressure

\(\rho\) Density

\(\sigma\) Stefan-Boltzmann constant

\(\sigma_k(n)\) Number of sites that each species \(k\) of phase \(n\) occupies

\(\varsigma_k\) External energy associated with species \(k\)

\(\bm{\tau}\) Viscous stress tensor

\(\Phi_{ij}\) Dimensionless tensor

\(\varphi_i\) Polar angle of surface element \(i\)

\(\chi_i\) Mole fraction of species \(i\)

\(\dot{\omega}_i\) Production rate of species \(i\) per unit volume of the composite

**Subscripts**

\(\text{in}\) Property at reactor inlet

\(\text{out}\) Property initial value

\(\text{out}\) Property at reactor outlet

\(\text{wall}\) Property at reactor wall

\(f\) Property of carbon fiber

\(g\) Property of gas-phase

\(s\) Property of pyrolytic carbon

\(ss\) Steady state

\(r\) Reference value

**Superscripts**

\(\ast\) Dimensional values
· Time derivative

e  Effective coefficient

T  Transpose
CHAPTER 1

INTRODUCTION

1.1 Background on Carbon/Carbon Composite Materials

The need for high performance materials hit a new peak in post World War II (WWII) America. The war theater, being the fertile opportunity that it was for testing the limits of the military machine, opened the gates of ingenuity of design, and thus the demand for high performance materials. Perhaps the first of the “advanced structural composites” was Boron fibers. Although versatile in their qualities, the Boron fibers had a relatively large diameter; this was an impediment in the manufacturing process since it is easier to control fabrics with geometrical structure of small diameter fibers. The make up of the fibers is made of different materials which causes thermal mismatches. In addition, the boron fiber manufacturing process was very costly [12].

The decade after WWII saw the manufacturing of many variations of fibers production, namely glass fibers. Even though glass fibers have a relatively lower strength than many other fibers, they were used extensively due to the low manufacturing costs. Nowadays glass fibers have higher strength than before however their brittleness at high temperature limits their usage.

Organic fibers were researched and developed in order to compensate for the brittleness of glass fibers. High strength and stiffness properties of carbon fibers
are mainly due to their unique nature of graphite crystalline anisotropic structure. Graphite crystal consists of stacked (sheet-like) graphene layers. In the direction of the graphene layer, carbon atoms are connected by strong covalent bonds of 400 $kJ/mol$, whereas in the normal direction to the layer, atoms are connected by weak van der Waals bonds. As a result the graphite tensile modulus in the layers direction is 1060 $GPa$, whereas it is 36.5 $Gpa$ in the normal direction to the layers [12]. This allowed for the temperament of the fibers to have both high strength and impact resistance. Therefore, carbon fibers have found use in the aerospace and aircraft composite industries.

In the early decade of 1950s, Carbon/Carbon (C/C) composites were synthesized to be used primarily as ablative materials. With the Space Shuttle programs in their embryonic stages, the need for thermal protection materials with specific properties was needed. These properties included, but were not limited to: light weight, high thermal shock resistance, low coefficient of thermal expansion, maintenance of strength at high temperatures, high impact resistance, and high stiffness. Although graphite possessed most of the crucial properties, it lacked high strength and stiffness especially in the normal direction to the graphene layer. That is the main deficiency in graphite. Overcoming that deficiency was achieved by introducing reinforced carbon matrix composites as they maintain their properties at high temperatures and are stable. As an example, pan-based carbon fibers had been produced in a way to compensate for the deficiency in graphite. Meanwhile in the plastics industry, fiber reinforced plastic technology was also advancing.

It was shortly after that the research and development in the US and Europe went into improvement constituent materials, i.e., carbon fibers, carbon matrix
precursors, and, development of fiber architecture technology such as multidirectional weaving technology and fabrication etc. [12].

Although the 1970s and early 1980s were prime years of C/C research and development, their use remained mainly in the aerospace domain. That was primarily due to their light weight, high density, and ablative properties.

Distinguished mechanical and thermal properties led to the necessity for the C/C industry to expand beyond the purview of the aerospace industry. Thus, both national and international companies in Europe and the US began manufacturing C/C composites for noble metals, glass industry tools, heating elements for the semiconductor industry, and crucibles to name a few applications.

With more global manufacturers coming on to the C/C scene in US and Japan, C/C possessed high quality pitch-based carbon fibers with very high stiffness and thermal conductivity. With applications increasing, so did the production, ultimately, leading to economic production. Since the 1960s, developments in the area of C/C composites are always strongly considered and implemented.

1.1.1 Characteristics of Carbon/Carbon Composites

Unique mechanical, thermal, as well as chemical properties of C/C composites are the main reasons behind their extensive use in industry [13]. The crystalline structure form of carbon (graphite) is the key factor behind its material characteristics. The structure can vary from fine to coarse, oriented or random, and with varying degrees of anisotropy.

Mechanical properties can be summarized as follows:

- High strength and stiffness at high and low temperatures.
- High Young’s modulus (failure occurs in the material at discontinuities due
to defects, pores, or impurities).

- Light weight as compared to other materials.

- Good toughness, where a reasonable work is required to propagate a crack.

- Good fatigue and creep properties.

- Stable friction performance, where the coefficient of friction shows limited variation with temperature compared to most other materials.

- Tailorable through control of fiber types, fiber architecture, matrix carbon and use of compounding of additives allows C/C composites to be manufactured to meet specific performance requirements.

- Anisotropy (since graphite is anisotropic, control of fiber orientation allows C/C composite properties, as well as friction and wear performance to be tailored).

Thermal properties can be summarized as follows:

- High thermal conductivity in the fiber direction.

- Low thermal expansion coefficient and hence low thermal stress.

- High thermal shock resistance since it can withstand very high temperatures of approximately 3000 K, as well as thermal fatigue cycles.

- High thermal heat capacity of approximately 709 J/kg/K.

Chemical properties can be summarized as follows:

- Low reactivity, and hence relatively high resistance to gasification (oxidation) below 400 °C.
• Adsorption (clean surfaces do not wet while oxidized and contaminated surfaces are highly wetted surfaces and subsequently lead to reduction in friction).

Comparison between the properties of fiber reinforced composites and those of other materials can be found in Table 1.1.

1.1.2 Applications of Carbon/Carbon Composites

The brake pad industry represents approximately 70% of the worldwide Carbon/Carbon C/C composites industry [1] as seen in Fig. 1.1. This is due to the development of high-speed, large-capacity airplanes during recent years, as well as the remarkable properties of C/C composites we have mentioned earlier. Other military applications include missile nose tips, thermal protection systems for the space shuttle, wing leading edges, and solid rocket motor throats. Civilian applications include furnace insulation, heating elements, X-ray targets, turbines blades, pistons, seal rings, connecting rods for diesel engines, hot press dies, tubes, fasteners, liners and plates, crucibles, molds, channels carrying molten glasses, hip prosthesis, microchips etc.

1.1.3 Components of Carbon/Carbon Composites

C/C composites are a class of synthetic materials that consist of highly-ordered graphite fibers (for reinforcement) embedded in a carbon matrix. The carbon matrix itself is brittle and cracks can propagate easily through it. Therefore, fibers act to strengthen the C/C composite. In C/C composites the fibers and matrix are both made of carbon. Each of them could have quite different structure as well as properties than the C/C composite. Many different precursor materials can be
used to produce carbon fibers, however rayon, polyacrylonitrile (PAN), and pitch are the most popular precursors. Rayon is a manufactured regenerated cellulosic fiber that was made first from inner bark of a mulberry tree. It was patented as “artificial silk” by George Audemars, a Swiss chemist, in 1855 [14]. PAN is a resinous fibrous, or rubbery, organic polymer that was found by Shindo, a Japanese researcher, in 1961 [15]. Pitch is the name for any number of highly viscous liquids, which appear solid, and consist of polyaromatic and cyclic aliphatic hydrocarbons. It is the heavy that product results from distillation of crude oil or coal tar that was discovered by Otani in the 1960s [16]. Among these precursors, PAN has proven to produce high strength fibers. Carbon fibers are obtained from previous precursors through multiple treatment processes. Briefly, these processes include carbonization of a precursor in an inert atmosphere from 1000 °C – 1500 °C,
followed by graphitization from $2000^\circ C - 3000^\circ C$ in an inert atmosphere. This process results in 100% carbon fibers.

The phase diagram of solid carbon shows that carbon starts melting at 100 bar and 4000 K. Therefore a carbon matrix cannot be produced through melting of carbon. However a carbon matrix, in which carbon fibers are embedded in, can be produced by pyrolysis of gaseous hydrocarbons through different manufacturing processes. Two processes used to form the carbon matrix are considered suitable commercially. Liquid phase impregnation with an organic resin or petroleum pitch, and chemical vapor infiltration/chemical vapor deposition (CVI/CVD) of pyrolytic carbon. These processes will be addressed in more detail in the next section.

It is worth mentioning that carbon fiber/carbon matrix surface interaction is a major factor in obtaining high or low strength C/C composites. Even though carbon fibers have high strength and stiffness, they are not of much use compared to C/C composites. A carbon matrix acts as a binder of these fibers (filaments) such that a final strong and stiff composite can be tailored and machined as desired. Therefore, weak carbon fiber/carbon matrix surface interaction leads to low strength composites since fibers can be separated from the matrix easily. On the other hand a very strong carbon fiber/carbon matrix surface interaction will result is a brittle composite that can be cracked upon loading. Hence, surface interaction should be managed correctly.

1.2 Manufacturing Techniques of C/C Composites

There are several techniques used in the manufacturing of C/C composites, however all these techniques can be summarized by essential steps. Those include
TABLE 1.1

COMPARISON OF PROPERTIES OF METALS, MONOLITHIC COMPOSITES, AND FIBER REINFORCED COMPOSITES [7].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Type of Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Steel</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>7.8</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m/K)</td>
<td>16.3</td>
</tr>
<tr>
<td>Thermal Expansion ($K^{-1} \times 10^{-6}$)</td>
<td>8.3</td>
</tr>
<tr>
<td>Tensile Strength (GPa)</td>
<td>1.3</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>200</td>
</tr>
</tbody>
</table>
the framework (substrate) formation, carbonization, densification, and heat treat-
ment (carbonization-graphitization) steps. Each of these steps will be discussed
in detail in the following sections. Fig. 1.2 summarizes these steps.

1.2.1 Framework (Substrate) Formation

A variety of substrates could be used according to fiber type, architecture, and
binder used. Fiber architecture is the spine of C/C composites since it determines
the characteristics and properties of the final product. Briefly, fiber architecture
could be classified, according to Ko [17], into four categories: discrete or continu-
ous (one-dimensional), planer interlaced (two-dimensional), and fully integrated
(three-dimensional). A wise decision should be made in the choice of carbon fiber
architecture according to the required application. Selected carbon fibers are ma-
chined and shaped according to the desired substrate form. This is followed by
carbonization (graphitization) of the carbon fiber substrate.

Subsequently, the carbon fiber substrate is ready for binding with a carbona-
ceous precursor such as a thermosetting resin (phenolic) or thermoplastic pitch.
The combined carbon fibers with desired resin are pressed under high temperature
then left to cool down to solidify the resin. Carbon fibers are already carbonized,
however the resin is not entirely carbon. Hence a carbonization step has to be
performed to convert the resin polymer matrix to carbon. This will be explained
in the next section.

1.2.2 Carbonization

During the carbonization process in an inert atmosphere between 800–1100 °C
[18], gases evaporate from the polymer matrix (substrate). This results in weight
Figure 1.2. C/C composite processing [1].
loss and shrinkage. Therefore, this step has to be done carefully since it affects
the characteristics of the final product due to the fiber/matrix surface interaction.
Normally, the substrate is heated very slowly, $5 - 10^\circ C/h$ and adjusted according
to the thickness of the substrate. Shrinkage of the substrate depends mainly on
the type of fiber used; however, it always results in a porous skeleton substrate.
Hence, a densification process has to be employed to fill in the pores. This step is
addressed in the next section.

1.2.3 Densification

Sometimes this process is called impregnation since the two most common den-
sification techniques are liquid-phase and gas-phase impregnation. In the former,
the substrate is submerged in an organic thermosetting liquid resin or thermo-
plastic pitch for several hours. Since the new matrix material is embedded in the
composite, carbonization is performed to convert the resin to carbon. This car-
bonization process usually occurs under a temperature between $1000 - 2880^\circ C$
and under different pressure ranges. This impregnation process is repeated from
4 - 16 times until the required density is achieved. The resulting C/C compos-
te from this process has a medium density. However uniformity is a remarkable
feature in the resulting composite due to impregnation with a liquid phase.

The gas-phase impregnation or CVI/CVD process, is different than the liquid-
phase impregnation. In this case it is possible to obtain a high density C/C
composite. In this process the porous skeleton substrate is densified by pyrolysis
of a hydrocarbon as a precursor. This process lasts a long time (of the order of a
month) at high temperature and low pressure, and results in nonuniform densifi-
cation, usually due to diffusion limitations. However, it can be applied to complex
substrate shapes, one can control the final substrate microstructure by varying infiltration parameters, achieve a highly densified substrate, and obtain very strong fiber/matrix surface interfaces [19]. There are different types of CVI/CVD processes, nevertheless all types follow the main steps. These types are isothermal, low pressure, high pressure, microwave, plasma enhanced, pulse etc. Isothermal CVI/CVD is the most commonly used, and commercially the most attractive, to the carbon disk brake industry and represents 70% of the worldwide C/C composites industry as mentioned previously. Therefore, we will explore this process in more detail in the next section.

1.3 Isothermal CVI/CVD

The leading manufacturing process in the aircraft brakes industry is CVI/CVD. In this process, porous preform brakes (substrates) are stacked vertically inside a reactor and are heated radiatively by the reactor wall which in turn is heated electrically. A precursor volatile hydrocarbon gas such as propane, methane, ethane, or benzene, is supplied at the bottom of the reactor. The hydrocarbon reacts and decomposes into numerous light and heavy hydrocarbons, as well as hydrogen and other products. These reactant hydrocarbon molecules infiltrate through the preform pores and react with the substrate surfaces as well as with themselves. Through this infiltration process, degradation due to interaction between hydrocarbon gas and solid substrate surfaces, result in pyrolytic carbon being deposited on the surfaces. Over time, the substrates fill in and become more dense and ultimately form carbon brakes. The remaining gas products leave the reactor from the top. Since the substrates are heated radiatively, the gases and substrates are approximately at a uniform temperature. This is the reason why the process is
sometimes referred to as an isothermal CVI/CVD process. The process lasts a long time since densification is limited by diffusion of gaseous hydrocarbons into the preforms.

There are two limits for such process. High temperatures result in reaction rates being much faster than the diffusion rates. This leads to a carbon deposition rate being larger on the outer preform surface than inner. This also creates a potential barrier that prevents gas from flowing from the outside to the inside of the core, leading to a crust being created on the outer substrate surface. In this case, the process is stopped so that the substrates can be mechanically ground to remove the crust to expose open pores again. Whereas low temperatures allow reactants to diffuse inside the preform pores before they react and subsequently carbon is deposited. For this reason, CVI/CVD reactors are usually operated at relatively low temperatures, pressures and flow rates, and result in very long processing times and subsequently high production costs. Therefore, there is a need to understand these two limiting conditions so that the deposition time can be minimized.

Multiphysical and multichemical phenomena are intrinsic in the above described CVI/CVD process. This includes the interaction between complex homogeneous gas phase reactions and complex heterogeneous surface/deposition reactions which depend strongly on the local substrate surface/volume ratio, or interfacial area density. Along with temperature and pressure, this ratio constitutes a very important parameter that has a large effect on the process [20]. Therefore, understanding the homogeneous gas-phase reaction mechanism as well as the heterogenous reaction mechanism is essential. In addition, heat transfer through radiation between the reactor wall and substrates as well as the mixed
convection gas flow may play important roles.

1.3.1 Objective

The major aim of this work is to obtain an accurate and reliable computational model of the CVI/CVD process. The work encompasses three major aspects that initially are studied independently, but ultimately are coupled to achieve the primary objective of the work. The first aspect includes the construction of a computational thermo-fluid model which includes radiative heat transfer. The second aspect accounts for the reaction chemistry model using methane (\(CH_4\)). The third aspect considers the carbon deposition/densification model within porous substrates.

1.3.2 Motivation

The significant beneficial gain that will be achieved from the development of the individual and combined models is the reduction of cycle time, and thus cost, during the manufacture of C/C composites of aircraft brakes. Therefore there is a need to construct a realistic and accurate model that enables one to maximize substrate densification rate, determine densification rate as a function of the parameters which it is most sensitive to, and examine properties of the exhaust gas.

1.3.3 Summary

The following chapters will be organized as follows. In Chapter 2 a comprehensive literature review will consider work that has been done regarding different phenomena appearing in the CVI/CVD reactor. Chapter 3 will present the most
general transport equations, constitutive equations, homogeneous gas-phase reaction mechanism, and heterogeneous surface reaction model. In Chapter 4 a detailed description of the numerical integration procedure and integration tools used are given. In Chapter 5 verification of the integration procedure as well as validation of different models used are discussed. Chapter 6 presents reactor simulations using a simple two step reaction mechanism as well as using other simplifying assumptions. Chapter 7 provides the results of a parametric study of the reactor taking into consideration the integration of all models used. In Chapter 8, conclusion are given and recommendations for further developments are suggested.
CHAPTER 2

LITERATURE REVIEW

The present work incorporates many physical phenomena within a CVD/CVI reactor, such as combined forced and natural (or mixed) convection using low Mach number (or non-Boussinesq) equations, multispecies reactive flow, detailed chemical kinetics, flow within porous media, heterogeneous reactions, and radiation between surfaces. These phenomena span a wide range of length as well as time scales. Thus, the objective of this section is to summarize the important work that has previously been done that deal with these different phenomena. The best way to present the previous work is to divide it between experimental work and numerical modeling. Numerical simulation models have to be validated through experimental results. The ultimate goal of all studies is to achieve a uniform density distribution within the substrates and to optimize the processing time and hence reduce cost. Therefore, whenever one examines the objective of any work concerned with CVD/CVI, either experimental or numerical, the focus is on one of the following topics: the effect of substrate surface area to reactor volume ratio, total pressure, hydrocarbon partial pressure, temperature, flow rate, and the use of different hydrocarbons (with different compositions) on the deposition rate and pyrolytic carbon microstructure. As regards numerical models, in addition to investigating the effects of the previous parameters, mathematical models for different parts have to be implemented. In other words, one requires a pore model
to represent the rate of filling during the infiltration process. Moreover, most model a homogeneous gas phase reaction mechanism as well as a heterogeneous surface reaction mechanism with appropriate rate kinetics parameters. In addition, a mathematical model that simulates reactive flow inside, as well as outside, the porous media is necessary.

2.1 Time and Length Scales in CVI Process

The CVD/CVI process contains many time and length scales. Inspired by the work of Vignoles et al. [2, 3], Fig. 2.1 shows the length and time scales respectively. Length scales vary from molecular scales of the order of nanometers to reactor dimension of the order of meters. Other length scales exist between these two disparate length scales, including the deposition layer thickness of the order of microns [21], pore size, fiber size, and preform size. On the other hand, time scales vary from those associated with electromagnetic waves of the order of less than an attosecond, to the deposition time scale of the order of months. Other time scales exist between these two disparate time scales, including the fast and slow chemical reactions rates, and conduction and convection time scales. A realistic model for the CVD/CVI process has to account for these scales. However, this cannot be realized since the span between the different scales is too large. Therefore, some fast scales are equilibrated to steady state. This is helpful in building a realistic model that can predict the final preform properties.

2.2 Methane Pyrolysis

An increase of the world natural gas reserves has resulted in substantial research devoted to natural gas. Natural gas consists mainly of methane (83% –
Figure 2.1. Length (top) and time (bottom) scales in CVI modelling [2, 3].

97%). Methane can be converted to C2 hydrocarbons (hydrocarbons with 2 carbon atoms) by two methods, oxidative coupling [22] or thermal coupling at a temperature above 1000°C. Oxidative coupling can be observed in combustion engines while thermal coupling (which will be given more attention in a later discussion) can be observed in static and dynamic reactors. These reactors have been studied extensively [23, 24]. Dynamic reactors are usually either shock tube reactors [25] or tubular flow reactors [26]. Thermal coupling of methane in a tubular flow reactor has been presented by Billaud et al. [26–28]. Reaction mechanisms are needed to simulate these dynamic reactors. Early remarkable works by Hidaka et al. [29–32] examine the thermal decomposition of different hydrocarbons.
(propyne and allene, propane, ethane, and methane) in shock tubes. These studies are considered to be the definitive studies of reaction mechanisms of methane pyrolysis. In these studies an elementary reaction mechanism for methane pyrolysis, diluted in argon, is presented and validated in the temperature range of 1400 – 2200 K and pressure range of 2.3 – 3.7 atm. A detailed kinetic model of autocatalysis on methane pyrolysis at 0.58 atm. and 1038 K has been presented by Dean [33]. The reaction mechanism consists of 44 reversible reactions and involves 25 species. A more recent version of the mechanism for the same conditions is presented by Li et al. [34]. An interesting reaction mechanism by Olsvik et al. [35, 36] is used to study hydrogen effects on the carbon formation in the gas phase in the temperature range of 1473 – 1773 K and atmospheric pressure. The same mechanism has been shown to work at the same pressure and at the temperature of 1273 K [37]. Norinage et al. [38] have recently proposed a reaction mechanism consisting of 230 species and 757 reactions. This mechanism is validated using experimental results [39]. The mechanism consists mainly of 5 combined reaction mechanisms: the comprehensive reaction mechanism of Wang and Frenklach [40] which consists of 90 species and 527 reactions, which accounts for hydrocarbons up to pyrene except odd hydrocarbons such as toluene and indene, the Marinov et al. [41] reaction mechanism that accounts for odd hydrocarbons, the Hidaka et al. [42] and Tsang [43] reaction mechanisms that account for C3 and C4 hydrocarbons (hydrocarbons with 3 and 4 atoms respectively), and the Richter et al. [44] reaction mechanism that accounts for large polycyclic aromatic hydrocarbons (PAH). The mechanism is validated for the pyrolysis of ethylene, acetylene, and propylene in the CVD/CVI of carbon at various pressure and temperature ranges, and residence time less than 2 seconds. A reaction mechanism presented
by Fincke et al. [45], consisting of 29 species and 87 reversible reactions, is used to simulate plasma pyrolysis of methane to hydrogen and carbon black. Matheu et al. [46, 47] have presented a new generation of reaction mechanisms. These authors have built a computational tool that generates systematically an accurate pressure dependent reaction mechanism for methane pyrolysis. However the number of species and reactions generated are quite large and it is difficult to reduce the resulting reaction mechanism. An elementary reaction mechanism for methane pyrolysis is given by Becker et al. [48].

While many reaction mechanisms have been published, it is extremely difficult to either model these reactions, or understand reaction paths and directions when the mechanisms are very large. Thus, a sensitivity analysis has been used to reduce the kinetic model for the carbon CVD/CVI process [9, 49]. Results from the reduced model are compared with experimental results [50, 51]. The experimental work is based on carbon deposition on a non-porous (smooth) surface. Moreover, in the above comparisons the authors use a combined methane mechanism with reaction rates from [43, 52, 53] in a commercial finite element code. The investigators account for the pressure fall-off effect (the effect of pressure on reaction rates) as due to using a unimolecular reaction mechanism for methane.

2.3 Major Parameters that Affect the Deposition Rate

Conclusions based on experimental work show that the most sensitive parameters to the deposition rate, and hence the carbon structure, are flow rate (residence time), temperature, pressure, and volumetric interfacial area density. Comprehensive reviews regarding the effects of initial partial pressure of hydrocarbon, residence time, type of hydrocarbon used, and temperature on the rate
of hydrocarbon deposition can be found in [54–56]. In [57–59] various pressures, temperatures, and substrate interfacial area densities are used to investigate the effect of these parameters on the carbon deposition rate. In the next sections we will discuss in more detail the work done regarding each of the above mentioned parameters.

2.3.1 Hydrogen Inhibition Effect

Hüttinger and co-workers [60] introduced fundamental aspects of this effect concerned with CVD/CVI. They state that methane is the ideal hydrocarbon to use for carbon deposition since it has the lowest molecular weight among all hydrocarbons, and the highest carbon/hydrogen ratio. Hence, it has the highest diffusion rate in Fick’s regime (outside the substrate) as well as in Knudsen’s regime (inside the substrate). Two hydrogen moles result from the decomposition of one mole of methane. In addition, the large surface area per unit volume inside the porous medium results in a higher hydrogen production rate inside the porous medium than outside. Hence, the hydrogen partial pressure inside the porous medium is higher than outside which results in a forced flow out of the porous medium that limits diffusion of hydrocarbons inside the porous medium. Subsequently, the Thiele modulus, which is the ratio of surface reaction rate to diffusion rate, increases. All hydrocarbons experience this hydrogen out flow problem but acetylene, hence it may be the ideal hydrocarbon [55]. A solution for this situation has been proposed by adding an excess amount of hydrogen. Generally an excess hydrogen amount reduces the homogeneous gas phase reaction rate as well as the heterogeneous one due to it inhibition effect. Regarding the gas phase reaction, this addition of hydrogen could be an advantage since it allows the hy-
drocarbon to diffuse through the porous substrate before it reacts with surfaces. Regarding surface reactions, hydrogen forms two types of bonds $C(H_2)$ and $C(H)$. The former is broken at $600^0C$ [61], therefore it is not important since a reactor usually operates near $1100^0C$. The second bond is stable at temperatures higher than $1000^0C$. This second bond causes blocking of active sites inside the pores [62, 63], and hence reduces the deposition rate. As a result, the forced flow out effect due to volume increase inside pores is reduced. Another factor to be taken into consideration is that hydrogen has the largest binary diffusion coefficient as compared with other diluents but helium [60].

Becker et al. [64] have studied the pyrocarbon steady state deposition rate as a function of hydrogen partial pressure. Different hydrocarbons such as acetylene, ethylene, and butadiene have been used at normalized pressure of 4 kPa, temperature of $1000^0C$, and residence time of 0.11 seconds. In [65] similar results at same conditions have been reported for propylene and benzene. All hydrocarbons experience a reduction in deposition rate due to increase in hydrogen partial pressure. These results differ from the results of Lucas et al. [66]. Starting with an enormous effect on benzene and PAHs to the weakest effect on acetylene (with the highest C/H ratio). Similar results for methane are reported in [48] for the same previous conditions except with temperature of $1100^0C$, since methane has lower reactivity than the other hydrocarbons. The previous discussion suggests the use of a hydrogen inhibition model by Becker et al. [67] of the Langmuir-Hinshelwood form [68–70]. For light (with low molecular weight) linear (carbon atoms are arranged in a straight line with no rings) unsaturated (have at least one double or triple bond) hydrocarbons such as acetylene, the hydrogen inhibition has less effect than ethylene, which is less unsaturated. Whereas for aromatic hydrocarbons,
such as benzene and PAH, the carbon inhibition is large due to the its molecular structure [67]. In other words, benzene does not have the ability to chemisorb on the pore surface with blocked sites, due to hydrogen inhibition, as much as acetylene and ethylene do. Therefore, at high hydrogen partial pressure, acetylene is considered the major deposited species whereas at low pressure benzene is the major deposited species. Hence, the limiting surface reaction step corresponds to the breaking of the carbon-hydrogen bond [71], not the dissociation of methane as indicated [72]. In addition, the deposition rate increases with the number of carbon atoms in the hydrocarbon. In fact benzene (and probably PAH) has the highest deposition rate if hydrogen is not added.

It is noted that PAH have limited contribution to the deposition rate due to their large molecular mass that limits their diffusion inside pores. An interesting conclusion reached in [67] is that the deposition on a surface from a certain hydrocarbon depends on the ability of that hydrocarbon to form an aromatic ring. Hydrogen inhibits some hydrocarbons in the gas phase from forming aromatic rings and hence reduces the deposition rate. In the case of methane as a precursor, the situation is more complicated since the surface reaction mechanism (associated with the hydrogen inhibition model) as well as gas phase reactions have to be considered together. Recent studies about the carbon/hydrogen bond dissociation energy can be found in [73, 74].

2.3.2 Heterogeneous Reactions

Heterogeneous reaction mechanisms, in contrast to homogenous mechanisms, are more complex and not as well understood. While this may be the case, experimental results show that gas-solid interactions have tremendous influence on the
deposition rate [58]. Therefore, in addition to a gas phase reduced mechanism, simple one step surface reaction mechanisms are used in [50, 51, 75]. In these mechanisms, a sticking coefficient which depends mainly on pressure and temperature [76], is used to express the deposition rate of the carbon on a non-porous surface. The sticking coefficient represents the fraction of the number of molecules that stick to the surface to the total number of molecules that impinge on the surface; simple models are derived from kinetic theory [77–80]. Chromatographic analysis of the gas shows the existence of a considerable number of hydrocarbon varieties, however based on [9, 49], the major species that contribute to the deposition arising from the methane reaction mechanism are acetylene, ethylene, benzene, and ethane. Moreover, recent work [48] suggests that acetylene, ethylene, and benzene are the main species responsible for deposition in the five step surface reaction mechanism used in [9, 49]. Detailed surface and gas-phase chemical kinetic mechanisms of diamond deposition are implemented by Frenklach et al. [81]. They assume equal reaction probabilities for similar gas-phase and gas-surface reactions. This assumption, explained by Gardiner [82] through kinetic gas theory, allows one to relate the gas reaction rates and surface reaction rates by the use of a sticking coefficient. Such sticking coefficient can be converted to a usual mass-action kinetic rate constant, as done in the SURFACE-CHEMKIN package [83]. Indeed, a general kinetic formalism for treating the details of heterogeneous reactions at a gas-solid interface can be found in [83, 84].

2.3.3 Hydrocarbon Initial Partial Pressure Effect

Several authors have studied the effect of hydrocarbon initial partial pressure as well as the total pressure on the deposition rate. Becker et al. [64] show that at
ambient total pressure, using ethylene as a hydrocarbon at 1000°C, increasing hydrogen partial pressure causes a weak exponential increase in the deposition rate at low residence time, while a strong exponential increase at large residence time. This suggests a first order reaction rate at small residence time while a higher order one at large residence time due to the contribution of other hydrocarbons. Similar results have been obtained with acetylene except that a weaker exponential dependence than ethylene is obtained. Benzene [65], is different than either acetylene or ethylene in that it experiences a linear dependence. For methane, at a temperature of 1100°C [48], the deposition rate increases exponentially at low methane initial partial pressure while it decreases continuously at high methane initial partial pressure. An interesting result is revealed by looking at the relationship between the partial pressures of acetylene, ethylene, and benzene with the partial pressure of methane. Acetylene and ethylene are consumed continuously at high methane partial pressure whereas benzene increases continuously. On the other hand, as noted previously, the deposition rate does not increase with the same rate as benzene does. This suggests that benzene is a dominant forming species, it cannot be chemisorbed on a surface. This conclusion is consistent with that in Section 2.3.1, where it was noted that high methane partial pressure causes high hydrogen partial pressure, and thus active sites are subsequently blocked to prevent benzene in being chemisorbed on the surface. Zhang and Hüttinger [85] have studied the carbon deposition rate as a function of substrate length at the temperature of 1100°C, total pressure varying between 10–90 kPa), and methane partial pressure varying between 5 – 20 kPa). This study shows that in general increasing the total pressure causes a decrease in the initial deposition rate. A similar result is suggested in [57, 86, 87]. In addition Benzinger and Hüttinger
[88–91] have studied the effect of methane partial pressure on the degree of pore filling.

2.3.4 Residence Time Effect

Residence time, unlike temperature and pressure, is usually different in almost every experiment. Becker and Hüttinger [48, 64, 65] have performed extensive studies on the carbon deposition rate as function of residence time using different hydrocarbons. They have shown that residence time has similar effect as noted with precursor partial pressures in that an exponential increase in deposition rate is observed with increasing residence time for all hydrocarbons. However, previous results are obtained using a cylindrical reactor as substrate.

The situation is quite different for a porous substrate. Zijun et al. [92] have simulated porous substrate as capillaries. They studied the effect of deposition rate through the capillaries as a function of residence time at various pressures and temperatures. They arrived at the conclusion that the deposition gradient from beginning of a capillary to its end increases as long as homogeneous gas phase reactions experience low residence time before arriving at the beginning of the capillary. Additionally, increasing the capillary length, increasing methane partial pressure, or decreasing residence time has the opposite effect. In fact by increasing of residence time, before arriving at the capillary mouth, the deposition gradient decreases and becomes negative after 2 seconds [93].

This inside-outside densification process is supported by the infiltration study of a porous substrate in [94], and a model in [95, 96]. In addition, Benzinger and Hüttinger have performed extensive studies on the effect of infiltration time.
2.3.5 Surface Area/Volume Ratio Effect

A cylindrical reactor with and without a honeycomb structure has been used in [97] to study the influence of deposition surface area/reactor volume ratio. Deposition rates have been done using diluent methane in argon as a source hydrocarbon at ambient pressure and 1100°C. In addition methane initial partial pressure has been varied up to 75 kPa and with residence time up to 1 second. Deposition rate using the honeycomb structure, not related to the substrate surface area (mol/hr), is much higher than it counterpart with honeycomb structure. However, the deposition rate related to surface area (mol/m² hr) for large residence time is much lower. When the free deposition volume exists, which has the same effect as small deposition surface area, hydrocarbons with higher carbon/hydrogen ratio will form rapidly in the gas phase. This in return causes high partial pressures of these hydrocarbons which results in a high deposition rate on the substrate surface. This increase continues with increasing residence time followed by decreasing in deposition rate since carbon is being consumed continuously. On the other hand if a small free deposition volume exists, which has the same effect as large surface area, radicals will chemisorb rapidly on the surface limiting hydrocarbon formation to C2 species. This causes a reduction in the deposition rate per unit area. Subsequently, since a pore with large diameter has surface/volume ratio greater than a pore of small diameter, a higher deposition rate is expected in the former [58]. This indicates that surface area/volume ratio (S/V), designated as a third parameter, has a significant effect on the deposition rate. Confirmation of the conclusions about the S/V ratio are found in [93, 98–100].

27
2.3.6 Temperature Effect

Temperature is the major parameter that affects the deposition rate. This due to the sensitivity of reactions, and hence, deposition rates to temperature variations. A model by McAllister et al. [101, 102] is used to explore reaction and diffusion of gases that occur simultaneously with carbon deposition inside porous media. This model is implemented in [103, 104] to predict the effect of operating conditions on the deposition rate inside a pilot-scale CVD/CVI reactor in which multiple substrates are densified simultaneously by carbon deposition from pyrolyzing hydrocarbon. It is found that temperature has the most significant impact on the uniformity of the deposition rate as well as the process time required. Hu et al. [20] have studied deposition rate in temperature range of $1050 - 1300^\circ C$, using various methane partial pressures, and various $S/V$ ratios. They confirm that temperature is a major parameter affecting the deposition rate. Similar results are reported in [71, 105].

2.3.7 Matrix Microstructure

Three major types of microstructure are revealed when a C/C composite is examined using polarized illuminated light: smooth laminar (SL), rough laminar (RL), and isotropic (ISO). These different microstructures result from different operating conditions. Pierson and Liebermann [106, 107] as well as Shi et al. [108] note that during the infiltration process, the carbon microstructure generally changes from SL to RL to ISO. In addition the ISO carbon can be obtained when acetylene is used as precursor, while laminar carbon is obtained when benzene is used. Lewis et al. [109] propose a model to predict the carbon microstructure during forced flow-thermal gradient chemical vapor infiltration (FCVI), whereas
Feron et al. [110] predict the transition from SL to RL during infiltration. It is found by Quli [111] that the initial substrate surface area has a notable effect on the matrix structure. Jyh-Ming explored [112] the increase in thickening rate followed by a decrease as the CVD temperature changed from $1100^\circ C$ to $1300^\circ C$ when methane and propane were used as hydrocarbon sources. Many studies on the relationship between the CVD/CVI parameters and the pyrolytic carbon microstructure have examined matrix deposition in fibrous carbon substrates [6, 20, 113–119].

2.4 Mathematical Models and Numerical Simulations

2.4.1 Low Mach Number Equations

One can simulate the problem using the compressible Navier-Stokes equations [50, 103, 120–123]. However, the numerical simulation of a flow containing propagation speeds from a few centimeters per second to acoustic speeds results in a very stiff system and requires a large computational cost. A typical alternative approach in convective flows is to use the Oberbeck-Boussinesq equations [124–126] which treat all properties as constants with the exception of a linear variation of density with temperature in the buoyancy term. These equations represent a generalization of the incompressible Navier-Stokes equations, but they only provide accurate solutions to flows in which small temperature variations are present. For gases, this limits temperature variations to approximately less than 30 K. In our study, the CVD/CVI process takes place in an environment where large temperature variations exist. Thus use of the Oberbeck-Boussinesq equations, as done in all previous non-isothermal CVD/CVI work, is inappropriate. Low Mach number equations, derived by Paolucci [127], account for large changes in temperature.
These equations have been used in simulating transient natural convection flow of a gas in a vertical slot with large temperature differences [128, 129], and to study the stability of such flows [130]. More recent studies that make use of low Mach number equations in the solution of natural convection in a closed cavity can be found in [131–133]. Moreover, a review of such flows and their numerical solution methods can be found in [134, 135].

2.4.2 Operator Splitting

It is evident in our problem that there is strong coupling between fluid flow, heat transfer, and reaction mechanisms inside as well as outside the porous substrates. This coupling leads to a large range of spatial and temporal scales being present in such the chemically reactive flow. Time scales may span many orders of magnitude from $10^{-10}$ s to the order of a month. The large span of time scales gives rise to a stiff computational system [136]. Moreover, spatial length scales have to be resolved from the finest scale, which may be of the order of $10^{-5} cm$ [137]. Thus, in addition to the stiffness difficulty, a large coupled system of equations has to be solved.

To overcome the temporal stiffness, different operator-splitting (OS) techniques are often used. OS techniques have been used extensively in combustion [138–141], air pollution [142–145], and hyperbolic flow [146–148] problems. Such techniques overcome stiffness inherent in the convection-diffusion-reaction equations by solving the convection-diffusion operator (convection-diffusion step) and reaction operator (reaction step) separately. This allows the use of different integration methods for each step. OS techniques can be classified as a sequential iterative (SI) approach or a sequential non-iterative (SNI) approach [149]. The SI
approach consists of an iterative procedure between the convection-diffusion and reaction steps [150–153]. The SNI approach consists of sequence of convection-diffusion steps followed by a reaction step [154, 155]. Reversing the integration order after each time step results in the symmetrical Strang-splitting algorithm [156, 157]. This algorithm is second order accurate in time if both steps are second order accurate. However the algorithm can be extended to higher orders [158]. Usually explicit integration methods are used for the convection diffusion step whereas implicit methods are used for the reaction step, which results in an implicit-explicit (IMEX) scheme [159–161]. The classical implementation of linear multistep methods to solve for the convection-diffusion step as well as the reaction step, leads to a reduction in the order of accuracy [151, 152]. To prevent this, a number of time sub-steps have to be computed within each step.

One big advantage of using OS techniques is the potential of doing parallel computations during the reaction step [151, 152, 162, 163]. This possibility arises due to local coupling of species concentrations at each grid point. The best known solvers that are usually used for the reaction step are LSODE [164, 165], DVODE [166], and VODPK [167, 168]. These are stiff solvers that use variable order, variable time steps. They have been collected recently in a package named SUNDIALS [169], a suite of nonlinear differential algebraic equation solvers.

Though OS techniques have many advantages, they have a disadvantage connected with the splitting error associated with operator decoupling and the subsequent use of appropriate boundary conditions. Several authors have analyzed this splitting error and the appropriate boundary conditions that should be used during splitting [149, 170–172].
2.4.3 Fractional Step Method

To overcome the difficulty associated with solving a large system of equations for the convection-diffusion step, different splitting procedures can be used [173, 174]. Here we focus on the fractional step algorithm. This algorithm is originally based on the pioneering work of Chorin [175–177] for solving incompressible flow [178–180]. The main difficulty arising in the incompressible flow equations is satisfaction of the divergence-free constraint imposed by the continuity equation. This amounts to an implicit coupling between continuity and the pressure appearing in the momentum equations [143]. Explicit schemes can be easily constructed so that the velocity field satisfies the divergence-free condition at each time step. However in our problem this will severely limit the size of the time step due to numerical stability restrictions. Implicit schemes can overcome such limitation on the time step, however difficulty arises in solving a large system of nonlinear algebraic equations which is computationally expensive.

A fractional step or projection method usually begins by solving the momentum equations, using the pressure field from the previous time step, to obtain a predicted velocity field that does not satisfy the continuity equation. Subsequently, using the predicted velocity field, a Poisson equation is solved to provide the pressure correction step necessary to assure that the new velocity field will satisfy the continuity equation. Finally the predicted velocity field is corrected using the new pressure field to obtain a velocity field that satisfy the continuity equation [181–184]. There is another procedure that is slightly different than previous one. In this procedure, the previous pressure field is not used in the computation of the predicted velocity field. Subsequently, the solution of the Poisson equation provides the full pressure, instead of a correction at the new time step.
The fractional step method is originally implemented on a staggered grid to prevent pressure oscillations, however it can also be applied on a non-staggered grid if special precautions was taken to prevent such oscillations [186]. In addition the method has been extended to solve variable density incompressible flows where now two constraints have to be satisfied: one associated with satisfying the continuity equation constraint and the other associated with satisfying the velocity divergence-free equation constraint [187–190]. Even though there are many advantages to the use of fractional step methods, there is a major disadvantage associated with the implementation of nonphysical boundary conditions that lead to errors. Extensive studies about discussing different procedures for dealing with boundary conditions can be found in [191–193].

Due to the fact that the pressure field in incompressible and low Mach number flows have elliptic character, the fractional step method is easily extended to low Mach number flows [128, 194–199]. In fact it has also been extended to all Mach number flows [200].

2.4.4 Reactive Flows using Fractional Step and Operator Splitting Methods

The OS and fractional step methods are attractive techniques for the solution of reactive flow problems. A number of researchers have used the combined methods to solve reactive flow problems using low Mach number equations [201–216].

2.4.5 Flow in Porous Media

Numerous models have been used to study flow within porous media [217]. Experimental and computational natural convection inside a heated cavity partially filled with porous media is studied in [218], where a non-Darcian model, including
Brinkman and Forchheimer terms, is used. In [219], a Darcy-Brinkman model with an additional inertial term is used to study the heat transfer and fluid flow inside a two-dimensional rectangular cavity partially filled with heat-generating porous media. The enhancement of heat transfer using a porous convection-to-radiation converter for laminar flow in a circular duct is studied using a Darcy model in [94], where the flow is taken to be hydrodynamically and thermally fully-developed. Stability criteria for convection in porous media (with or without chemical reactions) is considered in [220]. General reactive transport equations in porous media can be found in [221–224].

2.4.6 CVD/CVI Simulation

Other models have been used to study reactive flow inside porous media [225–228] to investigate the CVI of fiber-reinforced ceramic composites using a volumetric heating source (microwave power, a heating technique sometimes used for CVD/CVI). These studies emphasize the impact of power and exposure time at a given power level on the uniformity of porosity. The authors assume identical cylindrical fibres randomly oriented in three dimensional space. In [229–235], consideration is given to minimizing the infiltration time, and therefore also the cost, by determining the optimal pressure and temperature while using a one step reaction mechanism. Alexandre et al. [120, 121] formulate a three dimensional steady state model using a vorticity-velocity formulation to study gallium arsenide growth from a trimethylgallium and arsine source reactant. This model is useful in the manufacturing of thin solid films used in high speed digital circuits. McAllister et al. [103] developed a model for a pilot-scale CVI reactor using a simple reaction mechanism. Bammidipati et al. [50, 51] present a model, supported
by experiments, to account for the deposition rate on non-porous rod. Li et al. [10, 11] use a multi-step reaction mechanism, reduced from a larger elementary reaction mechanism, to simulate the deposition rate in carbon felt.

2.4.7 Pore Models

Pore topology changes continuously during the infiltration process. Hence the surface area density, tortuosity, permeability, and porosity also change. To simulate the deposition process quantitatively we have to provide a model which relates all of these quantities as they vary with infiltration time. Two types of pores have been observed in C/C composite matrix: micropores within fiber bundles (tows) and macropores between fiber bundles (cloth layers). Since it is difficult to characterize these pores mathematically, many authors develop different types of pore models. The single pore model is the one most commonly used [9, 49, 236, 237]. A random overlap model is also used in [101, 238–240]. Using this model, a Monte Carlo technique is applied to estimate effective Knudsen diffusion coefficients within the substrates, the permeability, and the accessible porosity as functions of total porosity. A bipore model, which accounts for micropores as well as macropores, is presented by Vaidyaraman et al. [241] in the development of a one dimensional model for FCVI of C/C composites. This model is improved and used by Li et al. [11] to obtain the surface area distribution of two dimensional carbon felt. Recent comprehensive reviews of various porus models can be found in [242–244].
2.4.8 Diffusion Models

Chemical reactions produce gradients in species concentrations which in turn results in molecular transport of species by flux diffusion. The simplest model of this flux diffusion, which is proportional to the negative linear gradient of species concentrations, is called Fick’s law for mass diffusion. The constant of proportionality is called the diffusion coefficient. Species can also be transported due to pressure gradients, temperature gradients (thermal diffusion or Soret diffusion), and other external forces such as gravity, electric field, or magnetic field. Once mass diffusion occurs, energy diffusion always follows as well. Energy diffusion is similar to mass diffusion in that it follows Fourier’s law for heat diffusion where the species gradient is been replaced by the temperature gradient which acts as driving force. Other driving forces causing heat diffusion is called thermo-diffusion or the Dufour effect [245]. Onsager reciprocal relations [246, 247] of thermodynamics provide the relationships between Soret and Dufour effects in linear irreversible processes [248, 249]. It should be noted that the main driving forces for mass diffusion and energy diffusion are species concentration gradients and temperature gradient respectively; hence the Soret and Defout effects are usually neglected [250].

Even though Fick’s law is used extensively, it is not possible generally to express the mass flux in multicomponent systems using the gradient of only one component [251]. There are two prevalent approaches in expressing diffusion in multicomponent systems; a generalized Fick’s law [252], where the mass flux is expressed as a linear combination of species concentrations gradients, and a generalized Maxwell-Stefan equation, where the mass flux is expressed as a linear combination of mass fluxes [249, 253]. The Maxwell-Stefan equation approach
is more attractive since use of generalized Fick’s law requires computation of $N^2$ co-factor determinants of size $(N - 1) \times (N - 1)$ and one determinant of size $(N - 1) \times (N - 1)$, where $N$ is the number of species [256].

Even with today’s computers, the estimation of multicomponents diffusion systems is quite expensive computationally for 2D and 3D applications. Therefore many simplified forms have been introduced to account for mass flux due to diffusion [257, 258]. The most attractive forms are based on mixture-average diffusion coefficients [84] and binary diffusion coefficients [257–259]. The importance of the binary diffusion coefficients approximation, which is relevant in the low-density regime, follows from the fact that they can be estimated from kinetic gas theory (see the Chapman-Enskog theory [260], Wilke and Lee formula [261, 262], Saksena and Saxena formula [263, 264], and Fuller-Giddings formula [265, 266]), and that for an ideal gas the Maxwell-Stefan diffusion coefficients are equal to binary diffusion coefficients to a first approximation [251, 252].

For diffusion inside porous media the situation is different. Pores sizes might approach the order of the mean free path. Hence the interaction between the molecules and the porous surface affects the diffusion much more than the interaction between the molecules themselves [267]. The Knudsen number, which provides the ratio between the mean free path and pore diameter [248], is larger than 10 for typical porous media [268]. Hence a combination of Fickian diffusion and Knudsen diffusion has to be considered [269].

Generally there are two approaches to model the coupling between convection and diffusion in porous media. The first approach is based on an advective-diffusive model (ADM) which depends on Fick’s law of diffusion [270]. The second approach is based on a dusty-gas model (DGM) which which makes use of kinetic
gas theory [271]. The DGM describes the coupling of fluxes, partial pressures, and partial pressure gradients in porous media. While such model is strictly valid only for homoporous media [272, 273] (that is, with uniformly sized pores), it has been recently shown [274] that it provides an excellent approximation for diffusion in heteroporous media as well. Similar models can be found in [275, 276].

2.4.9 Radiation

All previously mentioned CVD/CVI models have assumed isothermal conditions. Therefore the energy equation, and hence radiation between reactor wall and preforms, is not taken into consideration. This assumption needs further investigation since temperature is the most sensitive parameter to deposition rate as mentioned previously. This is due to the exponential dependence of reaction rates on temperature. In addition, reactor geometry and inlet conditions, such as a preheat zone, affect significantly the temperature field inside the deposition zone.

Inside a CVD/CVI reactor radiation is exchanged between the reactor walls as well as within the gas medium (volumetric radiation). Soot as well as gases such as carbon dioxide and water vapor are found to emit and absorb radiation energy considerably over a wide temperature range [277]. Other monatomic or symmetrical diatomic molecules such as nitrogen, oxygen, hydrogen, argon or helium can be considered as non-participating gases [278]. In fact different gas mixtures have different absorbing or scattering coefficients. The scattering coefficient is related to the inverse of the mean free path [279]. Hence in the low pressure regions the participating media effects can become negligible.

The effect of surface to surface radiation combined with convection and con-
duction has been considered for simple geometries by several authors. Effect of combined convection and radiation, in vertical tubes and channels, is considered in [280, 281]. The effect of radiation combined with natural convection in square cavities is studied in [282–285]. In addition, its effect has also been studied in a Rayleigh-Benard problem within a square enclosure [286].

Theoretically surfaces absorb and emit radiative energy at different wavelengths and in different directions. However for practical engineering purposes, gray surfaces are usually assumed. For porous surfaces the situation is more complicated. Porous media consist of small pores that behave as small cavities. Many reflections can occur within these cavities. A recent study that relate effective surface emissivity to different porosities can be found in [287].

2.5 Problem Statement

As evident from the previous sections, much research has been done on the CVD/CVI process. Therefore in this section we give a brief description of the model of present interest, the different physical and chemical aspects that are included in the model, and highlight the new contributions emanating from the proposed work.

We use the low Mach number equations to obtain the velocity, thermal, and species fields within the reactor. Since the low Mach number equations [127] are valid for the flow outside the porous disks, we modify these equations to account for the flow within the porous substrates. A Brinkman model is used to simulate the flow inside the porous substrates. Moreover radiation between the porous substrates and the reactor walls is considered as surface to surface radiation in the presence of non-participating media. In addition, we incorporate homogeneous
gas phase reactions as well as heterogeneous surface reactions within the porous substrates. Homogenous gas phase reactions for methane are documented in [48], while heterogenous surface reactions are given in [9, 49]. We use a Strang-splitting algorithm to solve for reaction and convective-diffusive terms in two sequential computational steps [156]. A fractional step method [185] is used to solve the resulting large coupled system for velocity, temperature, and pressure.

Major differences between the present model and other models considered in the literature include consideration of a large reduced reaction mechanism, which is important for the prediction of reaction paths as well as species concentrations inside the reactor, and coupled heterogeneous surface reactions to account for carbon deposition within the porous substrates. In addition, we account for radiation between the reactor wall and the porous substrates.

Lastly, it is expected that the model is considerably more computationally efficient than others considered in the literature, primarily due to the combined use of low Mach number equations in conjunction with the Strang-splitting algorithm and fractional step method.
CHAPTER 3

MATHEMATICAL MODEL

In this section we formulate in detail the governing equations, and initial and boundary conditions. Subsequently, we introduce the chemical kinetics and pore model.

3.1 CVI/CVD Reactor description

We consider the axi-symmetric reactor configuration previously presented in [288–290] and shown in Fig. 3.1. This is a commercial CVI/CVD reactor used in the industrial fabrication of carbon composite disk brakes. The disk brakes are produced by placing low-density (high-porosity) carbon preforms within the reactor. Subsequently, a hydrocarbon fuel is supplied at the bottom of the reactor which decomposes to produce gas phase radical species that react to form carbon particles. These particles infiltrate and are deposited inside the porous substrates via a surface reaction mechanism and thus reduce the porosity in the preforms. All other products of combustion leave at the top of the reactor. After a sufficiently long time, disk brakes of appropriate densities are removed from the reactor for further processing. The reactor extends vertically from $z = 0$ at the inlet to $z = L$ at the top, and from $r = 0$ at the centerline to $r = R$ at the cylindrical wall of the reactor. The hydrocarbon gas flows upwards through a preheat zone of length
$L_p$ and radius $R_{in}$, and enters the load zone in which the preform substrates are placed. Substrates are annular porous rings, as shown in the expanded view on the right of Fig. 3.1. Reactor dimensions are shown in Table 3.1 whereas substrates dimensions are shown in Table 3.2, Table 3.3, Table 3.4, and Table 3.5. Note that counting substrates start from bottom to top. A gap of (0.5 inches) exists between the bottom of the reactor and the first substrate as well as between all substrates.
**TABLE 3.1**

**REACTOR DIMENSIONS.**

<table>
<thead>
<tr>
<th>Reactor Dimensions</th>
<th>Symbols</th>
<th>Values (Inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>$L$</td>
<td>69.125</td>
</tr>
<tr>
<td>Radius</td>
<td>$R$</td>
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</tr>
<tr>
<td>Inlet Radius</td>
<td>$R_{01}$</td>
<td>5</td>
</tr>
<tr>
<td>Outlet Radius</td>
<td>$R_{02}$</td>
<td>12</td>
</tr>
<tr>
<td>Preheat Length</td>
<td>$L_p$</td>
<td>18</td>
</tr>
</tbody>
</table>

**TABLE 3.2**

**(FIRST TO FIFTH) SUBSTRATES DIMENSIONS.**

<table>
<thead>
<tr>
<th>Substrate Dimensions</th>
<th>Symbols</th>
<th>Values (Inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Radius</td>
<td>$S_{ir}$</td>
<td>5.86</td>
</tr>
<tr>
<td>Outer Radius</td>
<td>$S_{or}$</td>
<td>9.405</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_d$</td>
<td>0.99</td>
</tr>
</tbody>
</table>
TABLE 3.3

(SIXTH TO TENTH) SUBSTRATES DIMENSIONS.

<table>
<thead>
<tr>
<th>Substrate Dimensions</th>
<th>Symbols</th>
<th>Values (Inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Radius</td>
<td>$S_{ir}$</td>
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</tr>
<tr>
<td>Outer Radius</td>
<td>$S_{or}$</td>
<td>9.43</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_d$</td>
<td>1.04</td>
</tr>
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</table>

TABLE 3.4

(ELEVENTH TO FIFTEENTH) SUBSTRATES DIMENSIONS.

<table>
<thead>
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<th>Substrate Dimensions</th>
<th>Symbols</th>
<th>Values (Inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Radius</td>
<td>$S_{ir}$</td>
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</tr>
<tr>
<td>Outer Radius</td>
<td>$S_{or}$</td>
<td>9.48</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_d$</td>
<td>1.09</td>
</tr>
</tbody>
</table>
### Table 3.5

(Sixteenth to Thirtieth) Substrates Dimensions.

<table>
<thead>
<tr>
<th>Substrate Dimensions</th>
<th>Symbols</th>
<th>Values (Inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Radius</td>
<td>$S_{ir}$</td>
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<tr>
<td>Outer Radius</td>
<td>$S_{or}$</td>
<td>9.58</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_d$</td>
<td>1.335</td>
</tr>
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</table>

#### 3.2 Governing Equations

We use modified low Mach-number (non-Boussinesq) equations to simulate the flow within the reactor outside and within porous substrates. A detailed derivation of these equations is shown in A. The dimensionless equations are:

\[
\varepsilon_g \frac{\partial \rho_g}{\partial t} + \nabla \cdot (\varepsilon_g \rho_g \mathbf{u}_g) = \lambda \left( \frac{\rho_g}{\rho_s} - 1 \right) Dk \sum_{i=1}^{N_s} \omega_i; \quad (3.1)
\]

\[
\varepsilon_g \rho_g \left( \frac{\partial Y_i}{\partial t} + \mathbf{u}_g \cdot \nabla Y_i \right) = -\frac{1}{ReSc} \nabla \cdot \mathbf{J}_m^m + Dk \left( \omega_i + \varepsilon_g \sum_{j=1}^{N_s} \omega_j \right), \quad (i = 1, \ldots, N_g - 1) \quad (3.2)
\]

\[
\rho_s \frac{\partial \varepsilon_g}{\partial t} = -\lambda Dk \sum_{j=1}^{N_s} \omega_j; \quad (3.3)
\]

\[
\varepsilon_g \rho_g \left( \frac{\partial \mathbf{u}_g}{\partial t} + (\mathbf{u}_g \cdot \nabla) \mathbf{u}_g \right) = -\varepsilon_g \nabla \Pi + \frac{1}{Re} \nabla \cdot (\varepsilon_g \mathbf{T}_g) + \frac{\varepsilon_g}{Fr} \rho_g \mathbf{g} - \lambda \left( \frac{\nu_g}{ReDaK} + \frac{\varepsilon_g C_E |\mathbf{u}_g|}{Da \bar{\kappa} \bar{\nu}} \right) \frac{\varepsilon_g \rho_g \mathbf{u}_g}{2} \sum_{j=1}^{N_s} \omega_j; \quad (3.4)
\]
\[
\frac{\rho c}{\partial t} + \rho_g c_{p_g} \varepsilon_g u_g \cdot \nabla T = \frac{1}{P_e} \nabla \cdot (k \nabla T) - Dk \left( \lambda \sum_{i=1}^{N_s} h_i \dot{\omega}_i + \sum_{i=1}^{N_g} h_i \dot{\omega}_i \right) \\
- \frac{1}{ReSc} \sum_{i=1}^{N_g} J_i^m c_{p_i} \cdot \nabla T,
\]

(3.5)

corresponding to local balances of mass of the gas-phase mixture, evolution of \((N_g - 1)\) gaseous species, evolution of porosity inside the porous medium, gas-phase mixture linear momentum and energy equations, respectively. These equations generalize the standard low Mach number equations [127] and account for effects arising from the porous media and reaction terms [221]. Local thermal equilibrium between the solid matrix and the gas mixture inside the pores is assumed. We use the Stokes-stress constitutive equation, Ficksian law of diffusion in multicomponent gases to represent the mass diffusion flux for species \(i\) (neglecting Soret and DuFour effects) [291], gaseous species mass fraction summation to unity constraint, gaseous species mole fraction, gaseous mean molecular mass, thermal state equations for a mixture of ideal gases, specific enthalpy of species \(i\), gas mixture temperature-dependent specific heat, gas-phase mixture-averaged thermal conductivity [292], semi-empirical formulas for gas mixture dynamic viscosity [245, 261], rate of production of species \(i\) given by the law of mass action with Arrhenius kinetics with respect to unit gas volume or unit porous surface area, gas-phase or surface molar concentration of species \(k\) respectively, gas-phase or surface reaction rate constant of species \(j\), and rate of production of of gaseous or solid species \(i\) with respect to unit total volume (solid plus void). In dimensionless form, these relations are respectively given by:
\[ \tau_g = 2\mu_g \left( \nabla u_g + \left( \nabla u_g \right)^T - \frac{1}{3} I \nabla \cdot u_g \right), \tag{3.6} \]

\[ J^n_i = -\rho_g D^n_{i,M} \nabla Y_i, \tag{3.7} \]

\[ \sum_{i=1}^{N_g} Y_i = 1, \tag{3.8} \]

\[ \chi_i = \frac{M}{M_i} Y_i, \tag{3.9} \]

\[ M = \left( \sum_{i=1}^{N_g} \frac{Y_i}{M_i} \right)^{-1}, \tag{3.10} \]

\[ \rho_g = \frac{M}{1 + \left( \frac{\xi}{1-\xi} \right) T}, \tag{3.11} \]

\[ h_i = h^0_{i,f} + \int_{T_0}^{T} c_p(T')dT', \tag{3.12} \]

\[ c_{p,g} = \sum_{i=1}^{N_g} Y_i c_{p,i}, \tag{3.13} \]

\[ k_g = \frac{1}{2} \left( \sum_{i=1}^{N_g} \chi_i k_i + \frac{1}{\sum_{i=1}^{N_g} \chi_i k_i} \right), \tag{3.14} \]

\[ \mu_g = \sum_{i=1}^{N_g} \frac{\chi_i \mu_i}{\sum_{j=1}^{N_g} x_j \Phi_{ij}}, \tag{3.15} \]

\[ \dot{r}_i = \frac{M^*}{\Xi} \sum_{j=1}^{N_r} K_j (\nu''_{ij} - \nu'_{ij}) \prod_{k=1}^{N} [C_k]^{\nu''_k}, \tag{3.16} \]

\[ [C_k] = \begin{cases} \frac{\rho^* Y_k}{M^*_k}, & (k = 1, \ldots, N_g), \\ \frac{Z_k(n)Y_k}{\sigma_k(n)}, & (k = 1, \ldots, N_s), \quad \sum_{k=1}^{N_s(n)} Z_k(n) = 1, \end{cases} \]

\[ K_j = \begin{cases} a_j T^{\gamma_j} e^{-\frac{E_j}{RT}}, & \text{gas-phase/surface reaction,} \\ \left( \frac{\gamma_i}{1 - \gamma_i/2} \right) \frac{1}{(T_{tot})^m} \sqrt{\frac{RT}{2\pi M_i}}, & \text{surface reaction,} \end{cases} \]
\[
\dot{\omega}_i = \begin{cases} 
\varepsilon_g \hat{r}_i & \text{gas-phase reaction,} \\
S_v \hat{r}_i & \text{surface reaction,}
\end{cases} \quad (3.17)
\]

\[
\sum_{j=1}^{N_g} \dot{\omega}_j = - \sum_{j=1}^{N_s} \dot{\omega}_j, \quad (3.18)
\]

where \( \lambda \) is the binary parameter

\[
\lambda (r, z) = \begin{cases} 
1 & \text{if } (r, z) \text{ in porous medium,} \\
0 & \text{if } (r, z) \text{ in fluid,}
\end{cases} \quad (3.19)
\]

and \( \Phi_{ij} \) is a dimensionless matrix given by [293]

\[
\Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2. \quad (3.20)
\]

In the above equations, \( \mathbf{I} \) is the identity tensor, \( T^* \) and \( \rho^* \) are the dimensional temperature and density, and \( \Xi = \dot{\omega}_{CH_4_{in}} \) is the reference reaction rate estimated at reactor wall temperature and inlet properties. The specific heats at constant pressure of species \( i \), \( c_{pi} \), enthalpy of each gaseous species \( i \), \( h_i \), and reaction rate of species \( i \), \( \dot{\omega}_i \), is taken from Chemkin [294, 295] while viscosity, \( \mu_g \), and thermal conductivity, \( k_g \), of the gas mixture are taken from [291, 296].

Since there is no data available for the Ergun constant that is applicable to our problem, we take \( C_E = 0 \) in the linear momentum equation. In writing the above equations, we have used the following non-dimensionalizations (starred quantities are dimensional):

\[
\Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2. \quad (3.20)
\]
\[ \nabla = R \nabla^*, \quad t = \frac{t^*}{(R/u_{in})}, \quad u = \frac{u^*}{u_{in}}, \quad p = \frac{p^*}{\rho_{in} u_{in}^2}, \]
\[ \Pi = \frac{\Pi^*}{\rho_{in} u_{in}^2}, \quad \rho = \frac{\rho^*}{\rho_{in}}, \quad T = \frac{T^* - T_{in}}{T_{wall} - T_{in}}, \quad \mu = \frac{\mu^*}{\mu_{in}}, \]
\[ k = \frac{k^*}{k_{in}}, \quad J = \frac{J^*}{\sigma (T_{wall} - T_{in})^4}, \quad G = \frac{G^*}{\sigma (T_{wall} - T_{in})^4}, \]
\[ \tau = \frac{\tau^*}{\rho_{in} u_{in}^2}, \quad \dot{\omega}_i = \frac{\dot{\omega}_i^*}{\Xi}, \quad J_i^m = \frac{J_i^{m^*}}{\rho_{in} u_{in}}, \quad D_{iM} = \frac{D_{iM}^*}{D_{MM, in}}, \]
\[ h_i = \frac{h_i^*}{c_{pin}(T_{wall} - T_{in})}, \quad M = \frac{M^*}{M_{in}}, \quad c_p = \frac{c_{p^*}}{c_{pin}}. \tag{3.21} \]

The independent dimensionless physical parameters appearing in the problem are

\[ Fr = \frac{u_{in}^2}{g R}, \quad Re = \frac{u_{in} R}{\nu_{in}}, \quad Pe = \frac{\rho_{in} c_{pin} u_{in} R}{k_{in}}, \]
\[ Da = \frac{k_{ss}}{R^2}, \quad Sc = \frac{\nu_{in}}{D_{MM, in}}, \quad Dk = \frac{\Xi}{\rho_{in} u_{in}/R}, \]
\[ Bo = \frac{\rho_{in} c_{pin} u_{in}}{\sigma (T_{wall} - T_{in})^3}, \quad \kappa = \frac{\kappa^*}{k_{ss}}, \quad \xi = 1 - \frac{T_{in}}{T_{wall}}, \tag{3.22} \]

corresponding to the Froude, Reynolds, Peclet, Darcy, Schmidt, Damköhler, the Boltzmann numbers, respectively, whereas \( \kappa \) and \( \xi \) are the dimensionless permeability and temperature ratios, respectively. The dimensionless geometric parameters are

\[ r_i = \frac{R_{in}}{R}, \quad r_{o1} = \frac{R_{o1}}{R}, \quad r_{o2} = \frac{R_{o2}}{R}, \quad l = \frac{L}{R}, \quad l_p = \frac{L_p}{R}. \tag{3.23} \]
Figure 3.2. Sketch of boundary conditions.
3.2.1 Initial and Boundary Conditions

Assuming axi-symmetry, we consider the following dimensionless initial and boundary conditions as illustrated in Fig. 3.2:

\[ u_g(r, z, 0) = u_{ss}(r, z), \quad T(r, z, 0) = T_{ss}(r, z), \quad Y_i(r, z, 0) = Y_{ss}(r, z), \]
\[ \text{for } 0 < r < 1, \quad 0 < z < l, \quad (3.24) \]

\[ u_g(r, 0, t) = \left\{ 2u_m \left[ 1 - \left( \frac{r}{r_i} \right)^2 \right], 0 \right\}, \quad T(r, 0, t) = \left( \frac{r}{r_i} \right)^2, \quad Y = Y_{ss}, \]
\[ \text{for } 0 < r < r_i, \quad t > 0, \quad (3.25) \]

\[ u_g(r_i, z, t) = 0, \quad T(r_i, z, t) = 1, \quad \frac{\partial Y_i(r_i, z, t)}{\partial n} = 0, \]
\[ \text{for } 0 < z < l_p, \quad t > 0, \quad (3.26) \]

\[ u_g(r, l_p, t) = 0, \quad T(r, l_p, t) = 1, \quad \frac{\partial Y_i(r, l_p, t)}{\partial n} = 0, \]
\[ \text{for } r_i < r < 1, \quad t > 0, \quad (3.27) \]

\[ u_g(r_i, z, t) = 0, \quad T(r_i, z, t) = 1, \quad \frac{\partial Y_i(r_i, z, t)}{\partial n} = 0, \]
\[ \text{for } l_p < z < l, \quad t > 0, \quad (3.28) \]

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\[ u_g(r, l, t) = 0, \quad T(r, l, t) = 1 \frac{\partial Y(r, l, t)}{\partial n} = 0, \]

for \( r_{o1} < r < r_{o2}, \ t > 0, \tag{3.29} \]

\[ (-\Pi + \tau_n) \cdot n = 0, \quad \frac{\partial T(r, l, t)}{\partial n} = 0, \quad \frac{\partial Y(r, l, t)}{\partial n} = 0, \]

for \( 0 < r < r_{o1}, \ r_{o2} < r < 1, \ t > 0. \tag{3.30} \]

For the solution to be bounded, axi-symmetry conditions are employed as:

\[ \frac{\partial u_g(0, z, t)}{\partial n} = 0, \quad \frac{\partial T(0, z, t)}{\partial n} = 0, \quad \frac{\partial Y(0, z, t)}{\partial n} = 0, \] for \( t > 0. \tag{3.31} \]

\( u_m \) is the average velocity given by

\[ u_m^* = -\frac{\bar{Q}}{2 \left( \frac{1-\xi}{\xi} \right) \pi R_i^2 \left[ \frac{\ln(1-\xi)}{\xi} + 1 \right]}, \tag{3.32} \]

where \( \bar{Q} \) is the volumetric flow rate at ambient temperature at the inlet (not shown in Fig. 3.1). Since the deposition time is very long, we calculate the quasi-steady state velocity field \( u_{ss} \), temperature distribution \( T_{ss} \), and species mass fractions \( Y_{ss} \) at a fixed (initial) porosity, and then begin our unsteady simulation from such a solution.
3.2.2 Pore Structure Evolution Model and Effective Properties

There many models for surface/volume ratio evolution during infiltration time. A collection of some of these models is presented in [3] and in Table 3.6 and Fig. 3.3.

<table>
<thead>
<tr>
<th>Model</th>
<th>Expression</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$S_v = \frac{2}{r_f} \left[ (2 - \varepsilon_{g0}) \left( \frac{\varepsilon_{g}}{\varepsilon_{g0}} \right) - \left( \frac{\varepsilon_{g}}{\varepsilon_{g0}} \right)^2 \right]$</td>
<td>Polynomial [3]</td>
</tr>
<tr>
<td>2</td>
<td>$S_v = -\frac{2}{r_f} \varepsilon_g \ln \varepsilon_g$</td>
<td>Random capillaries [239]</td>
</tr>
<tr>
<td>3</td>
<td>$S_v = \frac{2}{r_f} \frac{\varepsilon_{g}}{\varepsilon_{g0}} (1 - \varepsilon_g)(\varepsilon^{-1}<em>{g0} \ln \left( \frac{\varepsilon</em>{g0}}{\varepsilon_g} \right) + 1)$</td>
<td>Random capillaries with hard-core porosity [297]</td>
</tr>
<tr>
<td>4</td>
<td>$S_v = \frac{2}{r_f} \left[ (2 - \frac{3}{2} \varepsilon_g) \left( \frac{\varepsilon_{g}}{\varepsilon_{g0}} \right) \left( 1 - \frac{\varepsilon_{g0}}{2} \right) \left( \frac{\varepsilon_{g}}{\varepsilon_{g0}} \right)^2 \right]$</td>
<td>Polynomial with half slope at $\varepsilon_{g0}$</td>
</tr>
<tr>
<td>5</td>
<td>$S_v = \frac{2}{r_f} (1 - \varepsilon_g) \frac{((-3/4)\pi \ln(1-\varepsilon_{g0}))^{2/3}}{((-3/4)\pi \ln(1-\varepsilon_{g0}))^{2/3} + \varepsilon_{g0}}$</td>
<td>Interpolation between spherical pores at small $\varepsilon_g$ and isolated cylinders at high $\varepsilon_g$</td>
</tr>
</tbody>
</table>

We assume that porous substrates consist of a fibrous population of randomly
Figure 3.3. Several models for $S_v$ as a function of gas porosity $\varepsilon_g$ during infiltration time [3]
overlapping capillaries of uniform size. The surface area of the gas/solid interface per unit volume of porous medium, $S_v$, and the evolution of the average pore radius, $r_p$, are estimated by Monte Carlo simulations [239, 298] and used in [231, 299, 300], corresponds to second model in Fig. 3.3,

$$S_v = \frac{-2\varepsilon_g \ln \varepsilon_g}{r_f} \ m^{-1}, \quad (3.33)$$

$$r_p = \frac{2\varepsilon_g}{S_v} \ m. \quad (3.34)$$

We define the effective specific heat per unit volume at constant pressure [231], and the effective conductivity inside the porous medium by [226]:

$$\rho c = \varepsilon_g \rho_g c_{pg} + (1 - \varepsilon_g) \rho_f c_f + (\varepsilon_{g0} - \varepsilon_g) \rho_s c_s, \quad (3.35)$$

$$k = \varepsilon_g k_g + (1 - \varepsilon_{g0}) k_f + (\varepsilon_{g0} - \varepsilon_g) k_s. \quad (3.36)$$

$p_f, p_s$ are densities of carbon fibers and pyrolytic carbon deposited, respectively. Carbon fibers density varies according to different architectures for different applications. In the present study $\rho_f^* = 1600 \ kg/m^3$ [301]. The pyrolytic carbon deposited density is taken to be $\rho_s^* = 2150 \ kg/m^3$. $c_f, c_p$ and $k_f, k_s$ are specific heats and thermal conductivities for carbon fibers and pyrolytic carbon deposited, respectively. These thermophysical properties are fitted to experiments by Beaugrand [302] on RVC-2000 carbon fiber felts and given by [3],

$$c_f^* = c_p^* = -42.4678 + 2.8516 T^* - 0.001 T^{*2} \ \ J/kg/K, \quad (3.37)$$

$$k_f^* = 1.1176 - 6.217 \times 10^{-4} T^* + 8.3 \times 10^{-7} T^{*2} \ \ W/m/K, \quad (3.38)$$

$$k_s^* = -3.466 + 0.0271 T^* - 2.05 \times 10^{-5} T^{*2} + 5.3 \times 10^{-9} T^{*3} \ W/m/K. \quad (3.39)$$

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The effective diffusivity $D_{iM}^e$ inside as well as outside the porous medium is expressed as [227, 303]:

$$D_{iM}^e = \left( \frac{1}{D_{iM}^e} + \frac{\lambda}{D_{i}^{ke}} \right)^{-1}, \quad (3.40)$$

where the effective binary diffusion coefficient of species $i$ in methane $D_{iM}^e$, the effective Knudsen diffusion coefficient $D_i^{ke}$, the binary diffusion coefficient of species $i$ in methane $D_{iM}^i$ for non-polar gases [8], and the Knudsen diffusion coefficient for species $D_i^k$ [268], are related by

$$D_{iM}^e = \frac{\varepsilon_g}{\eta^b} D_{iM}^i, \quad (3.41)$$

$$D_i^{ke} = \frac{\varepsilon_g}{\eta^k} D_i^k, \quad (3.42)$$

$$D_{iM}^i = 10^{-7} \frac{T^{+1.75} \left( \frac{1}{M_i^*} + \frac{1}{M_M^*} \right)^{1/2}}{p^* \left[ (\sum V_i^*)^{1/3} + (\sum V_M^*)^{1/3} \right]^2} \ m^2/s, \quad (3.43)$$

$$D_i^{ke} = \frac{2r_p^*}{3} \left( \frac{8\pi RT^*}{\pi M_i^*} \right)^{1/2} \ m^2/s, \quad (3.44)$$

where $\sum V_i^*$ represents the sum of atomic molar diffusion volumes of species $i$ (cm$^3$mol$^{-1}$) as given in Table 3.7, and $p$ is the pressure (atm). The bulk diffusion tortuosity, $\eta^b$, and Knudsen diffusion tortuosity, are given by

$$\eta^b = \varepsilon_g^{-2/3}, \quad (3.45)$$

$$\eta^k = 1.444 \varepsilon_g^{-1}. \quad (3.46)$$
TABLE 3.7
ATOMIC/MOLECULES DIFFUSION VOLUMES OF SOME SPECIES
[8].

<table>
<thead>
<tr>
<th>Species</th>
<th>C</th>
<th>H</th>
<th>N2</th>
<th>Ar</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16.5</td>
<td>1.98</td>
<td>17.9</td>
<td>16.1</td>
<td>2.88</td>
</tr>
</tbody>
</table>

The permeability, \( \kappa \), is given by [304]:

\[
\kappa^e = \frac{\varepsilon_g r_p^2}{8 \eta^v} \; m^2.
\] (3.47)

where \( \eta^v \), the viscous transport tortuosity, is given by [244]:

\[
\eta^v = 2.76 \varepsilon_g^{-2/3} (\ln \epsilon)^2.
\] (3.48)

Previous estimated tortuosities are accurate for low and medium properties but not for high gas porosities, which is the case in current model [243, 305, 306].

In writing the above relations as functions of porosity, we assume that the time scale for deposition process is much larger than time integration step (pseudo-steady state).

### 3.2.3 Fluxes Across Interfaces

The continuous mass fluxes across the porous substrates is satisfied by:

\[
\left[ \varepsilon_g J_{k}^{\rho} + \varepsilon_g \rho_g Y_k \right] \cdot n = 0, \quad (i = 1, \ldots, N_g)
\] (3.49)
where we have neglected the deposition reactive flux across the interface since the
deposition rate is small in the CVI/CVD process. In addition the normal stresses
as well as the dynamic pressure has to be continuous across the interface as,

\[
\begin{align*}
\left[ \tau_n \right] \cdot \mathbf{n} &= 0, \\
\left[ \Pi \right] &= 0.
\end{align*}
\]

(3.50)

(3.51)

The continuous heat fluxes across the porous substrates is satisfied by:

\[
\left[ -\frac{k}{Pe} \nabla T + \rho_g c_{pg} \varepsilon_g u_g T \right] \cdot \mathbf{n} = \frac{\varepsilon}{Bo} \left[ \mathbf{G} - \left( T + \frac{1 - \xi}{\xi} \right)^4 \right],
\]

(3.52)

\[
(1 - \varepsilon) \mathbf{G} = \mathbf{J} - \varepsilon \left( T + \frac{1 - \xi}{\xi} \right)^4,
\]

(3.53)

where \( \varepsilon \) is the effective emissivity of the porous medium, and \( Bo \) is the Boltzmann
number. \( \mathbf{G} \) and \( \mathbf{J} \) are the irradiation and radiosity vectors, respectively, related
by:

\[
G_i = \sum_{j=1}^{N_e} F_{ij} J_j,
\]

(3.54)

where \( N_e \) is the number of surface elements, and \( F_{ij} \) is the view factor expressed
as

\[
F_{ij} = \frac{1}{A_i} \int_{A_i} \int_{A_j} \frac{\cos \varphi_i \cos \varphi_j dA_i dA_j}{\pi \bar{r}_{ij}^2}.
\]

(3.55)

In the above equation, \( A_i \) and \( A_j \) are the areas of surface elements \( i \) and \( j \), re-
spectively, and \( \varphi_i \) and \( \varphi_j \) are the view angles to surface elements \( i \) and \( j \), and \( \bar{r}_{ij} \)
is the distance between the surface elements as illustrated in Fig. 3.4. The basic
assumption used in the above equations is that every surface element is diffusively emitting and reflecting, and is isothermal.

As can be noticed, we have selected reference values based on inlet conditions. These inlet conditions exist at the inlet of the pipe (not shown in Fig. 3.1) that supplies the reactor with $CH_4$, where the velocity is assumed to be one-dimensional. Moreover, we assume the following emissivity values:

$$\epsilon = 1.0 \quad \text{for reactor wall surfaces,} \quad (3.56)$$

and

$$\epsilon = 1.0 \quad \text{for inflow and outflow surfaces.} \quad (3.57)$$

whereas for the disk brake surfaces, the effective emissivity is related to the local porosity according to [287].
3.3 Kinetic Mechanisms

3.3.1 Homogeneous Reaction Mechanism

The gas-phase reaction mechanism inside the CVI/CVD reactor is fairly complicated to the extent that there is no complete reaction mechanism that describes the complete process. Usually researchers depend on experimental data to model reactions that may contribute in the CVI/CVD process. Narayana et al. [9] gathered a large set of reactions, 47 reversible reactions with 19 species, from the Gas Research Institute (GRI) database [307], based on species included in the mechanism of Becker et al. [59]. This large set of equations is subsequently reduced to a smaller set of equations using sensitivity and dimensional analyses based on the Damköhler number. In addition the authors arrange the dominant reactions in decreasing order of importance, as shown in Table 3.8. This kinetic mechanism represents the most general mechanism available and is estimated to be accurate within an error of 10%. This is the mechanism that is used for homogeneous gas-phase reactions in this work.

3.3.2 Heterogeneous Reaction Mechanism

As compared to homogenous reactions, heterogeneous reactions are much more complex. The complication is due to the fact that the mechanism includes many steps: transport of the reactant molecule to the surface by convection and/or diffusion, adsorption of the reactant molecule on the surface, reaction steps that involve various combinations of adsorbed molecules, the surface itself and gas-phase molecules, desorption of product molecules from the surface, and transport of the product molecules away from the surface by convection and/or diffusion.
### TABLE 3.8

<table>
<thead>
<tr>
<th>$j$</th>
<th>Reaction</th>
<th>$a_j$</th>
<th>$\beta_j$</th>
<th>$E_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + CH_3(+M) \rightarrow CH_4(+M)$</td>
<td>$1.27 \times 10^{16}$</td>
<td>$-0.63$</td>
<td>383.0</td>
</tr>
<tr>
<td>2</td>
<td>$H + CH_4 \rightarrow CH_3 + H_2$</td>
<td>$6.6 \times 10^{8}$</td>
<td>1.62</td>
<td>10840.0</td>
</tr>
<tr>
<td>3</td>
<td>$H + C_2H_2(+M) \rightarrow C_2H_3(+M)$</td>
<td>$5.6 \times 10^{12}$</td>
<td>0.0</td>
<td>2400.0</td>
</tr>
<tr>
<td>4</td>
<td>$H + C_2H_3 \rightarrow H_2 + C_2H_2$</td>
<td>$3.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>$H + C_2H_4(+M) \rightarrow C_2H_5(+M)$</td>
<td>$1.08 \times 10^{12}$</td>
<td>0.454</td>
<td>1820.0</td>
</tr>
<tr>
<td>6</td>
<td>$H + C_2H_4 \rightarrow C_2H_3 + H_2$</td>
<td>$1.325 \times 10^{6}$</td>
<td>2.5</td>
<td>12240.0</td>
</tr>
<tr>
<td>7</td>
<td>$H + C_2H_6 \rightarrow C_2H_5 + H_2$</td>
<td>$1.15 \times 10^{8}$</td>
<td>1.9</td>
<td>7530.0</td>
</tr>
<tr>
<td>8</td>
<td>$2CH_3(+M) \rightarrow C_2H_6(+M)$</td>
<td>$2.12 \times 10^{16}$</td>
<td>$-0.97$</td>
<td>620.0</td>
</tr>
<tr>
<td>9</td>
<td>$2CH_3 \rightarrow H + C_2H_5$</td>
<td>$4.99 \times 10^{12}$</td>
<td>0.1</td>
<td>10600.0</td>
</tr>
<tr>
<td>10</td>
<td>$CH_3 + C_2H_4 \rightarrow C_2H_5 + CH_4$</td>
<td>$2.27 \times 10^{5}$</td>
<td>2.0</td>
<td>9200.0</td>
</tr>
<tr>
<td>11</td>
<td>$C_2H + H_2 \rightarrow H + C_2H_2$</td>
<td>$4.07 \times 10^{5}$</td>
<td>2.4</td>
<td>200.0</td>
</tr>
<tr>
<td>12</td>
<td>$H + C_2H(+M) \rightarrow C_2H_2(+M)$</td>
<td>$1.0 \times 10^{17}$</td>
<td>$-1.0$</td>
<td>0.0</td>
</tr>
<tr>
<td>13</td>
<td>$C_3H_3 + C_2H_2 \rightarrow C_6H_6$</td>
<td>$2.87 \times 10^{14}$</td>
<td>0.0</td>
<td>820.0</td>
</tr>
<tr>
<td>14</td>
<td>$C_3H_4 + C_2H_2 \rightarrow C_6H_6$</td>
<td>$3.0 \times 10^{11}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>$C_3H_4 \rightarrow C_3H_3 + H$</td>
<td>$1.0 \times 10^{17}$</td>
<td>0.0</td>
<td>70000.0</td>
</tr>
<tr>
<td>16</td>
<td>$CH_3 + C_2H_2 \rightarrow C_3H_4 + H$</td>
<td>$6.74 \times 10^{19}$</td>
<td>$-2.1$</td>
<td>31590.0</td>
</tr>
<tr>
<td>17</td>
<td>$C_2H + C_2H_2 \rightarrow C_4H_3$</td>
<td>$1.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>18</td>
<td>$C_2H_2 + C_2H_2 \rightarrow C_4H_4$</td>
<td>$2.45 \times 10^{14}$</td>
<td>0.0</td>
<td>46400.0</td>
</tr>
<tr>
<td>19</td>
<td>$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H$</td>
<td>$2.0 \times 10^{12}$</td>
<td>0.0</td>
<td>5000.0</td>
</tr>
<tr>
<td>20</td>
<td>$C_2H + C_2H_4 \rightarrow C_4H_4 + H$</td>
<td>$1.21 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>21</td>
<td>$CH_3 + C_2H_6 \rightarrow C_2H_5 + CH_4$</td>
<td>$6.14 \times 10^{6}$</td>
<td>1.7</td>
<td>10450.0</td>
</tr>
<tr>
<td>22</td>
<td>$C_3H_4 + C_3H_3 \rightarrow C_6H_6 + H$</td>
<td>$2.2 \times 10^{11}$</td>
<td>0.0</td>
<td>2000.0</td>
</tr>
<tr>
<td>23</td>
<td>$C_2H_4(+M) \rightarrow H_2 + C_2H_2(+M)$</td>
<td>$8.0 \times 10^{12}$</td>
<td>0.4</td>
<td>88770.0</td>
</tr>
<tr>
<td>24</td>
<td>$C_3H_4 + C_2H_2 \rightarrow C_6H_6$</td>
<td>$4.47 \times 10^{11}$</td>
<td>0.0</td>
<td>30090.0</td>
</tr>
<tr>
<td>25</td>
<td>$C_3H_4 + C_2H \rightarrow C_3H_3 + C_2H_2$</td>
<td>$1.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>26</td>
<td>$H + C_2H_5(+M) \rightarrow C_2H_6(+M)$</td>
<td>$5.21 \times 10^{17}$</td>
<td>$-1.0$</td>
<td>1580.0</td>
</tr>
<tr>
<td>27</td>
<td>$H + C_2H_5(+M) \rightarrow C_2H_4(+M)$</td>
<td>$6.08 \times 10^{12}$</td>
<td>0.3</td>
<td>280.0</td>
</tr>
<tr>
<td>28</td>
<td>$H + C_2H_5 \rightarrow H_2 + C_2H_4$</td>
<td>$2.0 \times 10^{12}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

¹ Reactions that include third body (M) have pressure dependent rate constants. Either Lindemann [308] or TROE [309] fall-off forms can be used to express pressure dependency. The rate constant parameters are taken from the gri and checked against the NIST database [307, 310]. Units of $a_j$ are combination of mol, cm, s; units of $E_j$ are cal/mol.
Fig. 3.5. Furthermore, these steps are not well understood nor known in the literature for the methane/carbon interaction. However, most researchers make use of a sticking coefficient (probability) to express the net reaction rate of the above steps. The sticking coefficient is the ratio between the rate of adsorption of molecules by the surface to the rate of collision of molecules with the surface [77].

To predict the deposition rate within the porous substrates, a heterogenous reaction mechanism is required. There are two common ways to express surface deposition rate within porous media: sticking coefficients and Arrhenius forms.

Figure 3.5. Surface Reaction Mechanism.
TABLE 3.9

SURFACE REACTION MECHANISM FOR CARBON DEPOSITION

[9].

<table>
<thead>
<tr>
<th>j</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}_2\text{H}_2 + 2\text{C}(S) \rightleftharpoons 2\text{C}(S) + 2\text{C}(D) + \text{H}_2 )</td>
</tr>
<tr>
<td>2</td>
<td>( \text{C}_6\text{H}_6 + 6\text{C}(S) \rightleftharpoons 6\text{C}(D) + 2\text{C}(D) + 3\text{H}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>( \text{C}_2\text{H}_4 + 2\text{C}(S) \rightleftharpoons 2\text{C}(D) + 2\text{C}(D) + 2\text{H}_2 )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{CH}(S) \rightleftharpoons \text{C}(S) + \text{H}_2 )</td>
</tr>
<tr>
<td>5</td>
<td>( \text{H} + \text{C}(S) \rightleftharpoons \text{CH}(S) )</td>
</tr>
</tbody>
</table>

TABLE 3.10

STICKING COEFFICIENTS AT DIFFERENT PRESSURES [9].

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>10 ((1.3 \times 10^3 \text{Pa}))</th>
<th>40 ((5.3 \times 10^3 \text{Pa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>(5 \times 10^{-4})</td>
<td>(0.5 \times 10^{-4})</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>(4 \times 10^{-4})</td>
<td>(4 \times 10^{-7})</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>(4 \times 10^{-3})</td>
<td>(4 \times 10^{-4})</td>
</tr>
</tbody>
</table>

3.3.2.1 Sticking Coefficients

Since there is lack of information for such reactions, Birakayala et al. [9] have fit reaction rate parameters by comparing their results against experimental data of Bammidipati et al. [50]. This reaction mechanism is shown in Table 3.9 where \( \text{C}(S) \) represents carbon substrate whereas \( \text{C}(D) \) represents pyrolytic deposited carbon. Based on [9], acetylene, ethylene, and benzene are the major species
that contribute in the carbon deposition reaction. Sticking coefficients models are verified experimentally [50]. Their values for different pressures are shown in Table 3.10.

3.3.2.2 Arrhenius Form

Becker et al. [67] have presented a deposition model from methane, acetylene, ethylene, and benzene. That model is in the Langmuir-Hinshelwood form [68–70]. A hydrogen inhibition model is incorporated within this deposition model. For purpose of illustration, deposition from acetylene is presented.

Acetylene is chemisorbed on the free active sites,

\[ \text{C}_1() + \text{C}_2\text{H}_2 \xrightarrow{k_1,a} \text{C}_1(\text{C}_2\text{H}_2), \]  

followed by ring formation,

\[ \text{C}_1(\text{C}_2\text{H}_2) \xrightarrow{k_1,b} \text{C}_1(\text{H}_2), \]  

and formation of free active sites according to the reversible desorption of hydrogen,

\[ \text{C}_1(\text{C}_2\text{H}_2) \xrightarrow{k_2} \frac{1}{k-2} \text{C}_1() + \text{H}_2, \]  

where \( \text{C}_1() \) expresses the active sites on the surface, \( \text{C}_1(\text{C}_2\text{H}_2) \) expresses chemisorbed acetylene on active sites, and \( \text{C}_1(\text{H}_2) \) active sites that are blocked by chemisorbed acetylene. By assuming that ring formation is much faster than acetylene chemisorp-
tion, we can add the first two steps to get,

\[ C\infty(\cdot) + C_2H_2 \xrightarrow{k_1} C\infty(H_2), \]  
\hspace{1cm} (3.61)

Therefore, Eqns.(3.61) and (3.60) describe the whole process.

Total surface sites has to be conserved at any time, hence the site concentration have to be equal to active and blocked sites,

\[ C = C\infty(\cdot) + C\infty(H_2). \]  
\hspace{1cm} (3.62)

The reaction rates of Eqns.(3.61) and (3.60) can be written as,

\[ \dot{r}_1 = k_1 C\infty(\cdot) P_{C2H2}, \]  
\hspace{1cm} (3.63)

\[ \dot{r}_2 = k_2 C\infty(H_2) - k_{-2} C\infty(\cdot) P_{H2}. \]  
\hspace{1cm} (3.64)

At steady state, the rate of both equations have to be equal to the carbon deposition rate \( r_s \),

\[ \dot{r}_s = \dot{r}_1 = \dot{r}_2. \]  
\hspace{1cm} (3.65)

Combining Eqns.(3.61), (3.60) and (3.65), we get,

\[ \dot{r}_s = \frac{c k_1 k_2}{k_{-2} P_{C2H2}} + \frac{k_1}{k_{-2}} + \frac{P_{H2}}{P_{C2H2}}. \]  
\hspace{1cm} (3.66)

Li et al. [5] suggest that since the carbon-hydrogen bond is highly stable, \( k_2 \ll k_{-2} P_{C2H2} \). The assumption of \( k_2/k_{-2} P_{C2H2} \approx 0 \) is reasonable, hence we
Acetylene carbon deposition rate can be written as

\[
\dot{r}_s \approx c \frac{k_2}{k_{-2}} \frac{k_1}{[C_2H_2]} \frac{[H_2]}{C_2H_2}
\]  

(3.67)

where the first component represents the original deposition rate whereas the second component represents the hydrogen inhibition function. A similar derivation follows for other species. It is worth mentioning that in the case of using acetylene, ethylene, and benzene as precursors, the carbon deposition rate is as simple as in the previous derivation. However in the case of using methane as the precursor, the situation is more complicated since deposition happens from different species simultaneously. On the other hand, there is evidence that carbon deposition from methane is impossible, while from C1 species is possible [4, 311]. In other words methane has to decompose to other products so that it can deposit carbon.

The original deposition rates are presented in Table 3.11 [4, 311] whereas the hydrogen inhibition functions are fitted based on Becker’s exper-
TABLE 3.11

SURFACE REACTION MECHANISM RATE COEFFICIENTS [5, 10].

UNITS OF \( a_j \) ARE COMBINATION OF MOL, CM, S; UNITS OF \( E_j \) ARE J/MOL.

<table>
<thead>
<tr>
<th>( j )</th>
<th>Reaction</th>
<th>( a_j )</th>
<th>( E_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{CH}_4 \rightarrow \text{C(D)} + 2\text{H}_2 )</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{C}_2\text{H}_4 \rightarrow 2\text{C(D)} + 2\text{H}_2 )</td>
<td>( 7.24 \times 10^1 )</td>
<td>155000</td>
</tr>
<tr>
<td>3</td>
<td>( \text{C}_2\text{H}_2 \rightarrow 2\text{C(D)} + \text{H}_2 )</td>
<td>( 1.35 \times 10^1 )</td>
<td>126000</td>
</tr>
<tr>
<td>4</td>
<td>( \text{C}_6\text{H}_6 \rightarrow 6\text{C(D)} + 3\text{H}_2 )</td>
<td>( 4.75 \times 10^5 )</td>
<td>217000</td>
</tr>
</tbody>
</table>

Experimental data [67] and presented in [5]:

\[
I_{\text{CH}_4} = \frac{1.112}{1.112 + \frac{[\text{H}_2]}{[\text{CH}_4]}},
\]

(3.69)

\[
I_{\text{C}_2\text{H}_4} = \frac{1.104}{1.104 + \frac{[\text{H}_2]}{[\text{C}_2\text{H}_4]}},
\]

(3.70)

\[
I_{\text{C}_2\text{H}_2} = \frac{3.269}{3.269 + \frac{[\text{H}_2]}{[\text{C}_2\text{H}_2]}},
\]

(3.71)

\[
I_{\text{C}_6\text{H}_6} = \frac{0.589}{0.589 + \frac{[\text{H}_2]}{[\text{C}_6\text{H}_6]}}.
\]

(3.72)

Since there are insufficient experimental results, these functions are fitted at certain temperatures as shown in Fig. 3.6. These original surface deposition reactions as well as inhibition functions are used in the presented work.
Figure 3.6. Inhibition functions of various hydrocarbons (profile of \( CH_4 \) at 1373 K, others at 1273 K) as functions of hydrogen content [4].
CHAPTER 4

NUMERICAL ALGORITHM

In this chapter we provide a discussion of the numerical codes used in this work, and the numerical implementation of the low Mach number equations within these codes. In addition an integration procedure will be presented.

4.1 COMSOL versus FIDAP

We have used a finite element commercial computational fluid dynamics solver (FIDAP) to obtain the flow behavior and thermal field that occurs in the CVI/CVD reactor. However we have found that FIDAP is not flexible enough to be able to implement the porosity variation with time. Moreover, after much struggling and communications with FIDAP support personnel, we determined that the Strang-Splitting algorithm [156] could not be implemented within it. Therefore, a decision was made to use a different finite element commercial computational fluid dynamics solver, COMSOL, so that we could overcome FIDAP’s limitations. Subsequently, we have found that COMSOL is much more flexible and computationally faster than FIDAP.
4.2 Linking CHEMKIN to COMSOL

There is no systematic mechanism to include reactions within COMSOL 3.2. Hence we use CHEMKIN [294] and TRANSPORT CHEMKIN [291] to respectively provide information about reaction rates and transport properties. Linking CHEMKIN and TRANSPORT CHEMKIN to COMSOL is achieved through writing MEX files in MATLAB 7.0.

4.3 Implementation of Finite Elements

4.3.1 Formulation of the Discrete Problem

The objective of the finite element method (FEM) is to reduce the continuum problem (infinite number of degrees of freedom) described in Section 3.2 to a discrete problem (finite number of degrees of freedom) described by a system of ordinary differential equations. For purposes of clarity, we will restrict ourselves to a discussion of the discretization of the momentum and energy equations. The treatment of the species transport equations follows identically that of the energy equation.

The finite element procedure begins with the division of the continuum region of interest into a number of simply shaped regions called elements (e.g. triangles). Since an Eulerian description of fluid motion is used, these elements are assumed to be fixed in space. Within each element, the dependent variables \( T \), \( u_i \), and \( p \) are interpolated by functions of compatible order, in terms of values to be determined at a set of nodal points. For purposes of developing the equations for these nodal unknowns, an individual element may be separated from the assembled system. Within each element, the temperature, velocity and pressure fields are
approximated by,

\[ T(x, t) = \sum_{m=1}^{M_e} \theta_m(x) T_m(t) = \Theta^T T \]

\[ u_i(x, t) = \sum_{n=1}^{N_e} \psi_n(x) u_{in}(t) = \Psi^T U_i \]  \hspace{1cm} (4.1)

\[ \Pi(x, t) = \sum_{l=1}^{L_e} \phi_l(x) p_l(t) = \Phi^T \Pi \]

where \( T, U_i, \) and \( \Pi \) are column vectors of element nodal point unknowns and \( \Theta, \Psi, \) and \( \Phi \) are column vectors of the interpolation (or shape) functions. Herein the same basis functions are employed for all components of the velocity (and later for temperature).

Substitution of these approximations into the field equations and boundary conditions [312] yields a set of equations with residual errors,

\[ f_1(\Psi, U_i) = R_1, \]

\[ f_2(\Psi, \Phi, U_i, \Pi) = R_2, \]  \hspace{1cm} (4.2)

\[ f_3(\Psi, \Theta, U_i, T) = R_3, \]

where \( R_1, R_2, R_3 \) and are the residuals (errors) resulting from the use of the approximations of (4.1). The functions \( f_1, f_2, \) and \( f_3 \) correspond to the continuity, momentum, and energy equations, respectively. The Galerkin form of the Method of Weighted Residuals [313] seeks to reduce these errors to zero, in a weighted sense, by making the residuals orthogonal to the interpolation functions of each
element (that is, \( \Theta, \Psi, \) and \( \Phi \)). These orthogonality conditions are expressed by

\[
\begin{align*}
\langle f_1, \Phi \rangle &= \int_{\Omega_e} \Phi \cdot f_1 \, dx = 0, \\
\langle f_2, \Psi \rangle &= \int_{\Omega_e} \Psi \cdot f_2 \, dx = 0, \\
\langle f_3, \Theta \rangle &= \int_{\Omega_e} \Theta \cdot f_3 \, dx = 0,
\end{align*}
\] (4.3)

where \( \langle a, b \rangle \) denotes the inner product defined by

\[
\langle a, b \rangle = \int_{\Omega_e} a \cdot b \, dx,
\] (4.4)

and \( \Omega_e \) is the volume of the element. Then by using the Green-Gauss theorem and considering the boundary conditions to calculate integrals over the boundaries, we obtain the Galerkin weak form of the equations which can be combined into the single matrix equation,

\[
\overline{M}(U, T)\dot{V} + \overline{K}(U, T)V = \overline{F}(U, T),
\] (4.5)

where \( U = \{u, v\}^T \), \( V = \{U, T, \Pi\}^T \), \( \dot{V} \) indicates the time derivative of \( V \), \( \overline{M} \) contains coefficients of transient terms, \( \overline{K} \) contains the advection and diffusion fluxes as well as conservation of mass constraint, and \( \overline{F} \) contains applied boundary conditions as well as the volumetric forcing functions.

4.3.2 Choice of Interpolation Functions

The choice of interpolation functions used for the pressure variable in the mixed finite element model is further constrained by the special role that pressure plays. It has been shown, both numerically (see Reddy [314, 315] and Taylor and Hood
and theoretically (see Sani et al. [317, 318]) that, in order to prevent an overdetermined system of discrete equations, the interpolation used for pressure must be at least one order lower than that used for the velocity field (i.e., unequal order interpolation). This is called the Ladyzhenskaya–Babuska–Brezzi (LBB) condition [315].

In solving (4.5) the velocity and temperature are approximated using quadratic interpolation functions using a triangle element with 6 nodes, \((\psi, \theta) \in P_2\), given by

\[
\Psi = \Theta = \begin{pmatrix}
2\xi_1^2 - \xi_1 \\
4\xi_1\xi_2 \\
2\xi_2^2 - \xi_2 \\
4\xi_2\xi_3 \\
2\xi_3^2 - \xi_3 \\
4\xi_1\xi_3
\end{pmatrix},
\]

while the pressure is approximated using linear interpolation functions using a triangle element with 3 nodes, \(\phi \in P_1\), given by

\[
\Phi = \begin{pmatrix}
\xi_1 \\
\xi_2 \\
\xi_3
\end{pmatrix}.
\]

For triangles, the interpolation functions are expressed in terms of the natural barycentric (or area) coordinates \((\xi_1, \xi_2, \xi_3)\); note that the natural coordinates are not independent but related by \(\xi_1 + \xi_2 + \xi_3 = 1\) as illustrated in Fig. 4.1.
4.3.3 Solution Method

For spatial discretization, we have used $P_2/P_1$ triangular finite elements, which means a second-order spatial discretization is applied to all variables but pressure for which a first-order one is used.

For temporal discretization, we have used a second order backward difference scheme (BDF2) that allows us to use large time steps. Since we use an implicit time integration scheme, we use the linear equations solver UMFPACK [319], which is a package for solving unsymmetrical sparse linear systems. It is worth mentioning that explicit integration schemes may be used [23, 205]. In that case we do not need to use the linear equations solver, however in such case we would have to use extremely small time steps so as to guarantee the stability of the numerical scheme used. The decision to use implicit or explicit time integration schemes should be made based on the integration time and size of the problem. For fairly large problems implicit methods may lead to excessive CPU and memory requirements to solve the large linear system of equations.
After temporal discretization, (4.5) can be written in the form,

\[ KV = F. \quad (4.8) \]

where \( K \) is a function of \( V \). The above nonlinear system of equations has to be solved at each time step. The damped Newton method [320] is used to linearize and solve this nonlinear system through a series of iterations at each time step. This requires a solution of a linear system of equations within each iteration. Hence, UMFPACK [321], which is a highly efficient direct solver for unsymmetric systems, is used.

To advance the solution in time, we use the following algorithm. If \( V \) is the solution vector at a certain time step, and \( Q \) the solver’s estimate of the (local) error in \( V \) committed during this time step, then the step is accepted if

\[ \left[ \frac{1}{N_d} \sum_i \left( \frac{|Q_i|}{e_i + r_{tol} |V_i|} \right)^2 \right]^{1/2} < 1, \quad (4.9) \]

where \( e_i \) is the absolute tolerance for nodal point \( i \), \( r_{tol} \) is the relative tolerance, and \( N_d \) is the number of degrees of freedom.

4.4 Integration Procedures

4.4.1 Integration Procedure I

Here we describe the integration for one time step (\( \Delta t \)). We integrate reaction terms for scalar variables (\( T, Y_i, \varepsilon_g \)) through two half-time step integrations separated by a full-time step integration for the convective and diffusive terms. Each of the half-time steps, as well as the full-time step, are integrated through several fractional sub-steps. Let \( p \) be the total number of convection-diffusion frac-
tional sub-steps, hence \( p' = p/2 \) is the number of convection-diffusion fractional sub-steps in each half-time step. We denote the time step within each fractional sub-step as \( \Delta t' \). Note that the time step within each fractional sub-step could be different. We integrate the system of DAEs implicitly as follows:

1. Integration over a half-time step \( \Delta t/2 \) for reaction source terms using solutions from the previous time step. This step includes the solution of a large system of stiff ODEs corresponding to \( T, Y_i, \varepsilon_g \). Therefore, we use \textit{DVODE} [166], a stiff solver that uses variable order, variable time steps. The gas density is updated from the equation of state. The step can be expressed symbolically as:

\[
(p c)^{k+1} (T^{k+1} - T^k) = \int_{t^n}^{t^{n+1/2}} -Dk \left( \lambda \sum_{i=1}^{N_g} h_i \dot{\varepsilon}_i + \sum_{i=1}^{N_s} h_i \dot{s}_i \right) dt
\]

\[
\rho_g^{k+1} \varepsilon_g^{k+1} (Y_i^{k+1} - Y_i^k) = \int_{t^n}^{t^{n+1/2}} Dk \dot{\varepsilon}_i^{\text{hom}} dt, \quad (i = 1, \ldots, N_g - 1)
\]

\[
\rho_s (\varepsilon_g^{k+1} - \varepsilon_s^k) = \int_{t^n}^{t^{n+1/2}} -Dk \sum_{j=1}^{N_s} \dot{\varepsilon}_j dt,
\]

where \( \dot{\varepsilon}_i^{\text{hom}} \) is the production rate of species \( i \) per unit volume of the composite due to homogenous reactions only and,

\[
M^{k+1} = \left( \sum_{i=1}^{N_g} \frac{Y_i^{k+1}}{M_i} \right)^{-1},
\]

\[
\rho_g^{k+1} = \frac{M^{k+1}}{1 + \left( \frac{\varepsilon}{1-\varepsilon} \right) T^{k+1}},
\]

\[
(p c)^{k+1} = \varepsilon_g^{k+1} \rho_g^{k+1} c_{p_g}^{k+1} + (1 - \varepsilon_g) \rho_f c_f + (\varepsilon_g - \varepsilon_g^{k+1}) \rho_s c_s,
\]

\[
c_{p_g}^{k+1} = \sum_{i=1}^{N_g} Y_i^{k+1} c_{p_i}^{k+1},
\]

\[
c_{p_i}^{k+1} = c_{p_i}(T^{k+1}).
\]
2. Convection and diffusion terms are integrated for temperature, species, and porosity to predict $T$, $Y_i$, $\varepsilon_g$ over a full-time step in $p'$ sub-steps. We find that $p' = 4$ is enough for solution accuracy. In the first sub-step, we use the implicit Euler scheme and the solutions from (step 1). In the following sub-steps, we use a variable time step $BDF^2$ and the solution from the previous sub-steps to obtain the solution at $\Delta t$. Porosity remains constant throughout the convection-diffusion integration step since there are no convective nor diffusive terms in the porosity equation. The mixture gas density is subsequently updated using the equation of state. The solution of the equations is performed in a segregated manner by integrating one linear differential equation at a time:

\[
(\rho c)^{k} \left( \frac{a_1 T^{k+1} + a_2 T^k + a_3 T^{k-1}}{\Delta t'} \right) \quad = \quad \varepsilon_g^{k+1} - \varepsilon_g^{k}, \quad (4.18)
\]

\[
\tilde{\rho}_g \varepsilon_g^{k+1} \left( \frac{a_1 Y_i^{k+1} + a_2 Y_i^k + a_3 Y_i^{k-1}}{\Delta t'} \right) \quad = \quad F_T \left( \tilde{\rho}_g^{k}, \varepsilon_g^{k+1}, Y_i^{k}, u_g^k, T^{k+1} \right), \quad (4.19)
\]

\[
F_{Y_i} \left( \tilde{\rho}_g^{k}, \varepsilon_g^{k+1}, Y_i^{k+1}, u_g^k, T^{k+1} \right), \quad (i = 1, ..., N_g - 1) \quad (4.20)
\]
where,

\[ M^k = \left( \sum_{i=1}^{N_g} \frac{Y_i^k}{M_i} \right)^{-1}, \tag{4.21} \]

\[ \tilde{M} = \left( \sum_{i=1}^{N_g} \tilde{Y}_i \right)^{-1}, \tag{4.22} \]

\[ \rho_g^k = \frac{M^k}{1 + \left( \frac{\bar{\varepsilon}}{1-\xi} \right) T^k}, \tag{4.23} \]

\[ \tilde{\rho}_g = \frac{\tilde{M}}{1 + \left( \frac{\bar{\varepsilon}}{1-\xi} \right) T^{k+1}}, \tag{4.24} \]

\[ (\rho c)^k = \varepsilon_g^{k+1} \rho_g^k c_{p_{g_{i}}}^k + (1 - \varepsilon_g^0) \rho_f c_f + (\varepsilon_g^0 - \varepsilon_g^{k+1}) \rho_s c_s, \tag{4.25} \]

\[ c_{p_{g_{i}}}^k = \sum_{i=1}^{N_g} Y_i^k c_{p_{i}}^k, \tag{4.26} \]

\[ F_T \left( \rho_g^k, \varepsilon_g^{k+1}, Y_i^k, u_g^k, T^{k+1} \right) = -\rho_g^k c_{p_{g_{i}}}^k \varepsilon_g^{k+1} u_g^k \cdot \nabla T^{k+1} \]

\[ \quad + \frac{1}{P_e} \nabla \cdot (k^k \nabla T^{k+1}) \]

\[ - \frac{1}{ReSc_c} \sum_{i=1}^{N_g} J_i^m c_{p_{i}}^k, \nabla T^{k+1}, \tag{4.27} \]

\[ F_{Y_i} \left( \tilde{\rho}_g, \varepsilon_g^{k+1}, Y_i^{k+1}, u_g^k, T^{k+1} \right) = -\varepsilon_g^{k+1} \tilde{\rho}_g u_g^k \cdot \nabla Y_i^{k+1} \]

\[ \quad - \frac{1}{ReSc_c} \nabla \cdot \tilde{j}_i^m \]

\[ + D_k \left( \dot{\omega}_i^{het^{k+1}} + \lambda Y_i^{k+1} \sum_{j=1}^{N_s} \tilde{\omega}_j \right), \tag{4.28} \]

where \( \tilde{Y}_i \) is the most available updated value of \( Y_i^{k+1} \), otherwise it will be \( Y_i^k \), and \( \dot{\omega}_i^{het} \) is the production rate of species \( i \) per unit volume of the composite.
due to heterogenous reactions only. In addition,

\[ k^k = \varepsilon_g^{k+1} k_g^k + (1 - \varepsilon_g^0) k_f + (\varepsilon_g^0 - \varepsilon_g^{k+1}) k_s, \quad (4.29) \]

\[ k_g^k = \frac{1}{2} \left( \sum_{i=1}^{N_g} \chi_i \chi_i^k + \frac{1}{\sum_{i=1}^{N_g} \chi_i^k / \chi_i^k} \right), \quad (4.30) \]

\[ J_i^m = -\rho_g^k D_i e^k \nabla Y_i^k, \quad (4.31) \]

\[ \tilde{J}_i^m = -\tilde{\rho}_g D_i e^{k+1} \nabla Y_i^{k+1}, \quad (4.32) \]

\[ \tilde{\omega}_j = \tilde{\omega}_j(\tilde{\rho}_g, T^{k+1}, \tilde{Y}_i), \quad (4.33) \]

and \( a_1, a_2, \) and \( a_3 \) are given by \([322]\):

\[ a_1 = \left( 1 + 2\alpha \right) \left( \frac{1}{1 + \alpha} \right), \quad (4.34) \]

\[ a_2 = -(1 + \alpha), \quad (4.35) \]

\[ a_3 = \frac{\alpha^2}{1 + \alpha}, \quad (4.36) \]

\[ \alpha = \frac{\Delta t'^{k+1}}{\Delta t^k}. \quad (4.37) \]

3. The procedure in (step 1) is repeated to obtain \( T^{n+1}, Y_i^{n+1}, \rho_g^{n+1} \) and \( \varepsilon_g^{n+1} \).

4. Predict the intermediate velocity field, using \( BDF1 \) for the first time step and \( BDF2 \) the following time steps, for the pressure-split momentum equations using solutions from the previous time step for \( u, v, p \). In addition we use other variables from step 3.

\[ \rho_g^{n+1} \varepsilon_g^{n+1} \left( \frac{a_1 u_g + a_2 u_g^k + a_3 u_g^{k-1}}{\Delta t} \right) = F_u \left( \rho_g^{n+1}, \varepsilon_g^{n+1}, u_g^{n+1} \right) - \varepsilon_g^{n+1} \nabla \Pi_n, \quad (4.38) \]
where,

\[
F_u \left( \rho_g^{n+1}, \varepsilon_g^{n+1}, \bar{u}_g \right) = \frac{1}{Re} \nabla \cdot (\varepsilon_g^{n+1} \bar{\tau}_g) + \frac{\varepsilon_g^{n+1}}{Fr} \rho_g^{n+1} \nabla + \lambda Dk \frac{\bar{u}_g}{2} \sum_{j=1}^{N_s} \omega_j^{n+1} \nabla \cdot (\varepsilon_g^{n+1} \rho_g^{n+1} \bar{u}_g)
\]

(4.39)

5. Solve the Poisson equation for pressure using the intermediate velocity from the previous step:

\[
- \nabla \cdot \left( \varepsilon_g^{n+1} \nabla (\Pi^{n+1} - \Pi^n) \right) = \frac{a_1}{\Delta t} \left\{ \lambda \left( \frac{\rho_g^{n+1}}{\rho_s} - 1 \right) Dk \sum_{i=1}^{N_s} \omega_i^{n+1} - \varepsilon_g^{n+1} \left( \frac{\partial \rho_g}{\partial t} \right)^{n+1} - \nabla \cdot (\varepsilon_g^{n+1} \rho_g^{n+1} \bar{u}_g) \right\}
\]

(4.40)

\[
\left( \frac{\partial \rho_g}{\partial t} \right)^{n+1} = \frac{a_1 \rho_g^{n+1} + a_2 \rho_g^n + a_3 \rho_g^{n-1}}{\Delta t}.
\]

(4.42)

6. Perform a projection to obtain \( u_g^{n+1} \) by using the solution of pressure and intermediate velocities from the previous two steps:

\[
u_g^{n+1} = \bar{u}_g - \frac{\Delta t}{a_1 \rho_g^{n+1} \varepsilon_g^{n+1}} \nabla \left( \Pi^{n+1} - \Pi^n \right).
\]

(4.43)

This completes one time step.

4.4.1.1 Comments

1. Similar integration procedures are reported by Nicoud [194], Najm et al. [205, 206], and Lessani et al. [203]. The main difference is that the above
authors use explicit time integration methods.

2. There is no need to iterate over each sub-step in step 2 when we use a small time step. On the other hand, if we use a large time step, the solution procedure may become unstable. To overcome the stability problem, especially if large temperature variations exit in the domain, a predictor-corrector procedure can be employed [194, 203, 205, 206].

3. An alternate procedure to increase the time step allowed is to iterate over the linear system until a user specified error criterion is met. Usually the solution converges with 2 or 3 iterations. In addition, we introduce a different procedure that is similar to the previous one. The major difference is that the velocity and pressure fields (step 4) are integrated in the convection-diffusion step (step 2) with other variables. Therefore, the integration will start with half-time step as in step 1, followed by an integration of all variables for a full-time step (including velocity and pressure fields) as in 2. Afterwards, we repeat the previous two steps by integration for a full-time step. Finally we repeat step 1 by integration for a half-time step. This integration procedure is more efficient computationally that procedure I. However we find that solving the momentum equation together with the continuity equation at the end results in a more stable algorithm.

4. It is important to note that we can solve the coupled system of velocity and pressure fields instead of using a fractional step method. This mainly depends on the degrees of freedom that need to be accessed by the available memory.

5. The previous comment provides the main motivation to split the production
of each species $i$, $\omega_i$, into two parts. One part, $\omega_{i,\text{hom}}$, which is the production rate of species $i$ per unit volume of the composite due to homogeneous gas-phase reactions only. This part causes temporal stiffness due to gas-phase chemical reactions, hence, it is included in the reaction steps (step 1 and step 3). The other part, $\omega_{i,\text{het}}$, which is the production rate of species $i$ per unit volume of the composite due to heterogeneous surface reactions only, is included in the convection-diffusion step (step 2). Hence, the summation of Eqn.(4.20) over all gaseous species $N_g$ will be equivalent to the conservation of gaseous species equation (3.1).

6. The presented integration procedure allows for large number of species since one linear partial differential equation is solved at a time. However the total integration will be large as the number of species becomes large. Nevertheless, in the reaction step, we can ideally use a number of processors that is equal to number of nodes. This is due to the fact that the solution variables of the ODEs are only coupled at each node. On the other hand, in the convection-diffusion step, we can use the number of processors equal to the number of species. Therefore, applying a parallel computation to the above procedure can result in an extremely efficient integration scheme.

4.4.2 Integration Procedure II

The previous integration procedure is useful for obtaining transient as well as steady state solutions. However, since the deposition time scale is fairly large as compared to the other time scales, the previous integration procedure is not efficient computationally for obtaining the porosity at different times. Instead starting from the steady state solution at the initial porosity obtained by previous
procedure, we obtain the porosity at different times using the following quasi-steady procedure:

1. Integrate the porosity equation (3.3) for a certain time step.

2. Relax the other variables to a new steady state solution using the new porosity by the above integration procedure.

3. Repeat the previous two steps until a porosity corresponding to a dense felt is obtained. This corresponds to approximately one month in dimensional units.

Iterations within each time step could be required for stability considerations. In the current results we find that there is no need to iterate within each time step.
5.1 Introduction

In order to gain confidence that the numerical simulations produce accurate results, we first address issues concerning verification and validation (V&V) of computer program and results. V&V are systematic procedures to verify computational codes and validate them against experimental results.

Verification is the process that one uses to guarantee the correct implementation and accuracy of a mathematical model contained in the numerical code. Hence it does not address the issue of how close the mathematical model is to the real world [323]. Therefore, the ideal situation is for us to compare our numerical results with an analytical solution, which is not available in most cases. Hence, the method of manufactured solutions (MMS) [324] is employed where an analytical solution is constructed for use in verifying code accuracy [325, 326]. In this method an artificial solution field is proposed as a solution of the PDEs. Since the solution does not satisfy the PDEs, substitution of this solution in the PDEs results in source terms. These source terms are added to the righthand sides of the PDEs so that they then satisfy the manufactured solution. Subsequently, we have an analytical solution that satisfies the PDEs and BCs. Hence, by varying the spatial as well as temporal grid sizes we can measure numerical errors accordingly.
Validation is the process of exploring how close our model is to the real world. In other words, validation tests how well does the mathematical model represent the physics in problem. This is usually achieved by using available experimental data to compare with. Sometimes this can be difficult since the conditions in the experiment have to be the same as in the simulation. This requires available comprehensive experimental measurements for different parameters in different regions, especially at boundaries.

5.2 Verification

We introduce three types of verifications: of the equations used (low Mach number equations), of the numerical scheme used, and of integration Procedure II. Verification of low Mach number equations is performed by comparing with other numerical simulations, whereas verification of the numerical scheme is performed through a spatial and temporal convergence study. Verification of integration Procedure II is performed by solving a simplified problem in a coupled manner and compare its solution with that obtained using our integration procedure.

5.2.1 Verification of Low Mach Number Equations

To verify that the low Mach number equations are implemented correctly, we simulate the benchmark problem of a closed heat cavity in the Boussinesq limit [124, 125], as well as in the non-Boussinesq regime [128]. Hence, we compare simulation results of maximum velocity and its location with benchmark results. The vertical velocity distributions of Boussinesq limit as well as non-Boussinesq regime simulations can be seen in Fig. 5.1.

To facilitate the comparisons, the low Mach number equations were normal-
ized the same as in [128]. In addition the thermodynamic pressure equation is not solved and hence the thermodynamic pressure inside the cavity is considered constant due to its small effect. Subsequently, the Boussinesq results were obtained with the temperature difference parameter of 0.005, while a value of 0.6 is used in the non-Boussinesq regime. As can be seen from the figure, for $Ra = 10^5$ the maximum vertical velocity component at the vertical midsection of the cavity is approximately $v = 68.37$ at $x = 0.1$ in the Boussinesq limit. These values compare very well with the benchmark value [125] of $v = 68.59$ at $x = 0.094$. A similar agreement is seen in the low Mach number case (non-Boussinesq regime) when the asymmetric vertical velocity distribution is compared with that given in [128] for the same case. The maximum vertical velocity component near the hot wall at the vertical midsection of the cavity is approximately $v = 69.56$ at $x = 0.13$ in the non-Boussinesq limit. Again these values compare very well with simulation [128] of $v = 69.15$ at $x = 0.1$.

5.2.2 Convergence Study

Since the boundary conditions for the manufactured solution depends on time, use of Strang-Splitting algorithm will degrade the order of the scheme. This is explained extensively by Hundsdorfer and Verwer [322] (p.345) and [151] where corrected BCs may be used. Therefore the Strang-Splitting algorithm is excluded from the convergence study, since in our main problem we have only BCs that are not functions of time. Nevertheless the Strang-Splitting algorithm will be considered later during validation.

We take the domain for the manufactured solution to be square, $\Omega = (0, 1)^2$, with use Dirichlet boundary conditions. Eqns. (3.1), (3.4), (3.5) are employed
for nonporous media without source terms. However source terms are deduced using MAPLE [327] such that the proposed manufactured solution will satisfy the PDEs. Species equations are not considered since they are similar to the energy equation. In addition we take $\mu_g = k_g = Re = Pr = 1$.

We propose the exact solution of $u, v, p, T, \rho$ to be:

\begin{align*}
  u &= \sin(x + \omega t) \sin(y + \omega t), \quad (5.1) \\
  v &= 2 \cos(x + \omega t) \cos(y + \omega t), \quad (5.2) \\
  p &= \sin(x - y + \omega t), \quad (5.3) \\
  T &= \tanh(x + y + \omega t) + 3, \quad (5.4) \\
  \rho &= \frac{1}{T}. \quad (5.5)
\end{align*}
For simplicity we take $\omega = 1$. For measuring error, we employ the $E_\infty$ norm. Which is defined as:

$$E_\infty = \max_{i,j} |e_{i,j}|,$$

(5.6)

where $e_{i,j}$ is the local error which is defined as:

$$e_{i,j} = u_{\text{num}}(x_i, y_i) - u_{\text{ex}}(x_i, y_i),$$

(5.7)

and where $u_{\text{num}}$ is the numerical solution, $u_{\text{ex}}$ is the exact or analytical solution, and $(x_i, y_i)$ corresponds to a nodal point.

5.2.2.1 Spatial Convergence Study

For the spatial convergence study we use Lagrangian $P_2/P_1$ quadratic square finite elements. We use a mesh with an equal number of elements in each coordinate direction. Six different meshes are used with 10, 20, 40, 80, and 120 elements in each coordinate direction. The time step is kept at $10^{-4}$ so that the temporal discretization error is negligible. Fig. 5.2 shows that the spatial convergence slope for $u$ is slightly greater than 2. This is not the case at small $\Delta x$ where the spatial discretization error is very small as compared to temporal discretization error.

5.2.2.2 Temporal Convergence Study

A fixed spatial mesh of 100 elements in each coordinate direction is considered during the temporal convergence study so that the spatial discretization error is negligible. Time steps are taken to be $5 \times 10^{-4}$, $8 \times 10^{-4}$, $10^{-3}$, $1.25 \times 10^{-3}$, $2 \times 10^{-3}$, $4 \times 10^{-3}$, $5 \times 10^{-3}$, $6.25 \times 10^{-3}$, $10^{-2}$, $2 \times 10^{-2}$, and $10^{-1}$. Fig. 5.3 shows
that the temporal convergence slope for $u$ is approximately 2. This is not the case at small $\Delta t$ where the temporal discretization error is very small as compared to spatial discretization error.

![Spatial convergence study](image)

**Figure 5.2.** Spatial convergence study.

### 5.2.3 Verification of Integration Procedure II

Our objective in this section is to verify integration Procedure II. Therefore we use a simplified non-stiff gas-phase reaction mechanism so that the equations in Sec. 3.2 can be solved in a coupled manner to be compared with integration Procedure II. This work is presented in [328].

We consider the symmetric reactor configuration in [6, 94, 329] which con-
sists of carbon felt, with 42 mm (length) × 16 mm (width) × 40 mm (height), as shown in Fig. 5.5, inside the reactor shown in Fig. 5.4 (only half of the reactor is shown). The felt is divided into 16 blocks for the purpose of measuring different properties at different locations within the felt. The carbon felt has low density (high porosity). Subsequently, pure methane is supplied at the inlet of the reactor, where it decomposes to produce gas phase radical species that react to form carbon particles. These particles infiltrate and are deposited inside the porous felt via a surface reaction mechanism and thus reduce the porosity in the felt. Carbon particles grow inside the felt through nucleation growth. All other products of combustion leave at the outlet of the reactor. We choose operating conditions to be as in the experiment [6], except that the residence time (based on felt height) is 0.05 sec instead of 0.1 sec as compared to the experiment. This causes the felt to be densified in a month instead of 120 hrs as compared to experiment so that the
process can be compared to the commercial one. In addition the boundary conditions is shown in Fig. 5.6. A parabolic distribution for temperature at the inlet is considered so that the energy equation is solved instead of assuming isothermal conditions as in the experiment. Therefore the operating conditions are as the follows: the reactor wall temperature is $1368 \, K$, the pressure is $22.5 \, kPa$, and the initial porosity is $0.775$.

Figure 5.4. Sketch for the reactor and the felt.
Li et al. [11] present a multi-step simplified gas reaction mechanism for methane that is fit to the experimental data of Becker et al. [48, 65, 67]. In addition they present a heterogeneous reaction mechanism that incorporates hydrogen inhibition effects [5, 10]. The gas phase reaction mechanism is shown in Fig. 5.7 and given in Arrhenius form in Table 5.1, whereas the heterogeneous reaction mechanism is given in Arrhenius form in Table 3.11.

Since our objective in this study is to verify the accuracy of the quasi-steady time integration procedure (Procedure II), we have neglected the radiation heat
Figure 5.6. Boundary conditions of the reactor.

\[ (-\Pi + \tau_e) \cdot n = 0 \]

\[ \frac{\partial T}{\partial n} = 0 \]

\[ \frac{\partial Y_i}{\partial n} = 0 \]

\[ u = 0 \]

\[ \frac{\partial u}{\partial n} = 0 \]

\[ \frac{\partial T}{\partial n} = 0 \]

\[ \frac{\partial Y_i}{\partial n} = 0 \]

\[ u = 0 \]

\[ T = 1 \]

\[ \frac{\partial Y_i}{\partial n} = 0 \]

\[ u = \frac{(x - r_f)(x - 1)}{(r_f^2 + r_f + 1) - \frac{(r_f^2 + 1)^2}{2} + r_f} \]

\[ T = \left( \frac{x - r_f}{1 - r_f} \right)^2 \]

\[ Y_{CH_i} = 1 \]
Fig. 5.7. Multi-step reaction mechanism [5].

Flux for simplicity. Figs. 5.8, 5.9, 5.10 present the porosity variations after 2, 16, and 30 days obtained by the quasi-steady and fully coupled computational procedures. As can be noticed the solution obtained by the quasi-steady integration procedure is very close to that of the coupled solution. The success of our integration procedure lies behind the fact that the deposition time scale is fairly large as compared to the other time scales present in the problem. In fact the disparity between these scales become larger as the porosity approaches zero. This fact is supported by the results shown in Fig. 5.11 and Fig. 5.12 where the average bulk density and average porosity are estimated at different infiltration times. These figures suggest that an adaptive time step will be more efficient than a uniform time step. This should be achieved by using a small time integration step for porosity at early infiltration times followed by larger porosity time steps as the porosity approaches zero.
Figure 5.8: Porosity after 2 days.
Figure 5.9: Porosity after 16 days.
Figure 5.10: Porosity after 30 days.

(a) Fully coupled solution  
(b) Quasi-steady (step=1 day)  
(c) Quasi-steady (step=2 days)
Figure 5.11. Average bulk density as a function of time.

Figure 5.12. Average gas porosity as a function of time.
TABLE 5.1

MULTI-STEP GAS-PHASE REACTION MECHANISM RATE COEFFICIENTS [11]. UNITS OF $a_j$ ARE COMBINATION OF MOL, CM, S; UNITS OF $E_j$ ARE J/MOL.

<table>
<thead>
<tr>
<th>$j$</th>
<th>Reaction</th>
<th>$a_j$</th>
<th>$\beta_j$</th>
<th>$E_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$CH_4 \rightarrow \frac{1}{4}C_2H_4 + H_2$</td>
<td>$2.86 \times 10^9$</td>
<td>0</td>
<td>251648.0</td>
</tr>
<tr>
<td>2</td>
<td>$C_2H_4 \rightarrow C_2H_2 + H_2$</td>
<td>$1.17 \times 10^{15}$</td>
<td>0</td>
<td>355230.0</td>
</tr>
<tr>
<td>3</td>
<td>$C_2H_2 \rightarrow \frac{1}{3}C_6H_6$</td>
<td>$2.44 \times 10^2$</td>
<td>0</td>
<td>79925.0</td>
</tr>
<tr>
<td>4</td>
<td>$C_6H_6 \rightarrow \frac{1}{3}C_{12}H_{10} + \frac{1}{2}H_2$</td>
<td>$3.0 \times 10^4$</td>
<td>0</td>
<td>107370.0</td>
</tr>
</tbody>
</table>

5.3 Validation

In this section we present two validations results. One is concerned with the gas-phase reaction mechanism whereas the other is concerned with the deposition of a 2D carbon fiber preform with a $0/0/90/90^\circ$ fiber structure.

5.3.1 Validation of Gas-Phase Reaction Mechanism

It is very difficult to validate CVI/CVD reactor results against experimental results for many reasons. CVI/CVD reactors are usually associated with carbon deposition on reactor surfaces which affects homogeneous gas-phase hydrocarbons concentrations. The higher the rate of carbon deposition the larger is the effect. On the other hand there is no known satisfactory theory that can describe carbon deposition in a CVI/CVD reactor from methane. In addition, deposition rates are usually interpolated from experimental results at certain conditions. Therefore to test a homogeneous gas-phase reaction mechanism, we have to test it under low conversion conditions of methane. This is usually done by using a diluent, such as
helium, argon, nitrogen, or hydrogen, that limits carbon deposition [67]. In addition there is always uncertainty about the determination of residence time as well as temperature and pressure inside the reactor [85]. However the most sensitive parameter that could affect the measured data is the temperature field throughout the reactor [26]. Usually an effective temperature, which has to be lower than the maximum measured temperature throughout the reactor, is considered [37].

Numerical validation is done by simulating the experiments of Olsvik et al. [35, 37]. In these experiments a plug flow reactor with inner diameter 9 mm and length 1200 mm was used. In the first experiment, a mixture of methane and helium (He : CH₄ = 2 : 1) was supplied into the reactor at the constant temperature of 1273 K and atmospheric pressure. Whereas in the second experiment, a mixture of methane and hydrogen (H₂ : CH₄ = 2 : 1) was supplied into the reactor at the constant temperature of 1773 K and atmospheric pressure. Residence time was varied by varying flow rates. Conversion of methane, yield, and selectivity of products were measured as a function of residence time using a gas chromatograph. Even though the experiment can be simulated in 1D coordinates, we have chosen to simulate it in 2D axi-symmetric coordinates. That allows us to validate our gas-phase reaction mechanism used in Table 3.8, as well as our governing equations, with the exception of the energy equation and the deposition model. The convergence of methane, the yield of a product CₐH₉, and the selectivity of a product CₐH₉ are defined by,

\[ \text{Conv}_{CH₄} = \frac{\bar{Q}^\text{in}_{CH₄} - \bar{Q}^\text{out}_{CH₄}}{\bar{Q}^\text{in}_{CH₄}}, \]  \hspace{1cm} (5.8)

\[ \text{Yield}_{CₐH₉} = \frac{\bar{Q}^\text{out}_{CₐH₉}}{\bar{Q}^\text{in}_{CH₄}}, \]  \hspace{1cm} (5.9)

\[ \text{Sel}_{CₐH₉} = \frac{\text{Yield}_{CₐH₉}}{\text{Conv}_{CH₄}}. \]  \hspace{1cm} (5.10)
where $Q_{CH_4}^\text{in}$ is the feed rate of methane, $Q_{CH_4}^{\text{out}}$ is the flow rate of methane from the reactor, and $Q_{C_nH_m}^{\text{out}}$ is the flow rate of product from the reactor. As mentioned in Sec. 3.3.1, the gas-phase reaction mechanism used is reduced from a larger reaction mechanism using sensitivity analysis and dimensional analysis based on the Damköhler number at a temperature of 1373 $K$ and pressures of 20 – 40 torr [9]. However, the reaction mechanism’s reaction rates variation with pressure is incorporated through Lindemann [308] or Troe [309] coefficients. The validation is done at atmospheric pressure (760 torr) according to the experiment’s operating pressure.

In both simulations, a temperature different than the measured one is used. This is because the difference between wall and center of the reactor increases by increasing the flow rate. Therefore in these experiments an effective temperature was determined to be between 40 – 50$^\circ C$ in [35, 37]. It is worth noting that the GRIMech3.0 mechanism [307] produces very similar results to our simulation.

Figs. 5.13, and 5.14 show good agreement between simulations and experimental results. Two important points should be made clear about the validation. The first validation corresponds to a residence time of approximately 2 sec., however in the simulation of the reactor a larger residence time is observed. Additional experiments should be performed for larger residence times to investigate the validity of the reaction mechanism in such cases. In the second validation, while even though we are most interested in data for acetylene, ethylene and benzene as they are species most responsible for deposition, there is insufficient data available at the moment to validate the benzene [330]. Hence, additional investigations should be pursued in the future to validate benzene formation in the gas phase.
Figure 5.13. Conversion (%) of $\text{CH}_4$, and yields (%) of $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, and $\text{C}_3\text{H}_2$ using $\text{He}: \text{CH}_4 = 2 : 1$ feed composition, $T_{\text{sim}} = 1263$ K, and $p = 1$ atm. Solid lines are simulation results whereas symbols are experimental data.

Figure 5.14. Conversion (%) of $\text{CH}_4$ and selectivities (%) of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$ using $\text{H}_2: \text{CH}_4 = 2 : 1$ feed composition, $T_{\text{sim}} = 1723$ K, and $p = 1$ atm. Solid lines are simulation results whereas symbols are experimental data.
5.3.2 Validation of Deposition of a Carbon Fiber

We validate the deposition model using Zhang [6] isothermal isobaric experimental reactor shown in Fig. 5.4. This experiment was run for 120 hrs at pressure of 30 kPa, temperature of 1368 K, initial porosity of 0.775 using 2D carbon fiber preform shown in Fig. 5.5 with a 0/0/90/90° fiber structure. The flow rate was adjusted, assuming a fully developed flow rate, such that residence time is 0.1 sec. according to preform height. Unfortunately there is insufficient information about the preheat zone length. Therefore we have assigned an arbitrary length. However it turns out that the preheat zone affects the deposition rate significantly. On the other hand the temperature inside the reactor was assumed to be constant during the experiment. That had been tested by flowing pure argon and measuring the temperature inside the reactor using a thermocouple. Before the experiment started, the thermocouple was removed to not block the flow outlet. Thus, the temperature was not measured during experiment. A significant radial and axial temperature gradient is reported in a similar reactor [85].

In the current simulation, we use all equations specified in Sec. 3.2 except energy equation. We set the pyrolytic carbon density to 2200 kg/m³, fiber density to be 1720 kg/m³ and initial carbon fiber radius of 4µm. In addition we use the stiff gas-phase reaction mechanism in Table 3.8, the surface reaction mechanism in Table 3.11 and model 3 for for surface to volume ratio from Table 3.6. The boundary conditions is similar to what we use for verification in Sec. 5.2.3 as shown in Fig. 5.6.

Fig. 5.15 shows a comparison between the average bulk density from experimental results [6] and from the simulation. Even though the results look different, it reveals the inside-outside densification gradient phenomenon at different height.
(a) Bulk density as a function of the distance from the preform at various heights of $r = 5\, mm$; $r = 15\, mm$; $r = 25\, mm$; $r = 35\, mm$, at methane pressure of 30 kPa and temperature of 1368 K, from [6].

(b) Bulk density as a function of the distance from the preform at various heights of $r = 5\, mm$; $r = 15\, mm$; $r = 25\, mm$; $r = 35\, mm$, at methane pressure of 30 kPa and temperature of 1438 K, from simulation.

Figure 5.15: Comparison between experimental results [6] and simulation for estimating average bulk density ($gcm^{-3}$).
in the preform. That appears because we consider the hydrogen inhibition model in the deposition model. As can be seen simulation in Fig. 5.16, the maximum bulk density is about 2.0 \( g/cm^3 \), whereas the maximum bulk density in the Zhang experiment [6] was about 2.2 \( g/cm^3 \). In fact Zhang et al. [85] reported a significant change in pyrolytic carbon density during densification and the center and surface of the preform. At the moment there is no model that can predict that pyrolytic carbon density change with time and space as necessary. That could be one of the reasons why we have a low carbon bulk density in our simulation. Another reason that we noticed is the diffusion coefficient that depends mainly on Knudsen diffusion and tortuosity model. This affects the diffusion mass flux into the preform and hence deposition rate. As we mentioned above the preheat zone also affects deposition rate since it affects species evolution. Moreover the residence time is very small. That cause deposition to be extremely sensitive to species concentrations. To conclude, more experimental results are needed to examine the deposition model.
Figure 5.16. Bulk density after 120 hrs.
CHAPTER 6

TRANSIENT SOLUTION OF THE CHEMICAL VAPOR DEPOSITION/INfiltrATION REACTOR USING A SIMPLE REACTION MECHANISM

The work in this chapter is a continuation of the work reported in [288] who considered only the heat transfer and fluid flow in a test furnace. The work in this chapter has been presented in [289]. We simulate the heat transfer and the fluid flow inside the reactor shown in Fig. 3.1. We use the equations show in Sec. 3.2 with some simplifications:

- We use the Brinkman model to account for flow inside the porous medium and we assume that the porosity is a function of time only. Therefore we neglect convective terms for flow inside the porous media.

- The divergence free term in the stress tensor constitutive equation 3.6, is set to zero.

- We set the dimensionless diffusivity, thermal conductivity, and dynamic viscosity inside the reactor as well as within the porous media to unity.

- The volume fraction is assumed to be the same as the area fraction of the porous media.
We make use of Fick’s law in obtaining a constitutive equation for the barycentric diffusion mass flux of species and neglect Soret and DuFour effects [245].

Knudsen diffusion within the porous media is not considered.

A simple two-step reaction model is included to study the chemical vapor infiltration (CVI) inside as well as outside the porous substrates (reactor volume). The first reaction describes the decomposition of the hydrocarbon ($CH_4$) outside the porous substrate, while the second reaction describes the deposition mechanism inside the porous substrates.

The interphase reaction source term in the momentum equation is neglected.

The radiation between the reactor surface and brake surfaces is not considered.

The density, specific heat, and thermal conductivity of pyrolytic carbon is taken to be equal to carbon fibers.

The coverage is taken to be $\theta_i = 0$ so that the sticking probability is constant.

$\sigma_s(1) = Z_s(1) = 1$ since we have only one solid specie (carbon).

The Dupuit-Forchheimer relationship ($U_g = \varepsilon_g u_g$) which relates the pore velocity of the gas $u_g$ to the Darcian velocity $U_g$ within the porous media is used.

The hydraulic diameter theory of Carman-Kozeny is used to calculate the permeability $\kappa$. This model gives reasonable results for media that consists
of spherical particles whose diameters fall within a limited range [217]:

\[ \kappa = \frac{2 \times 10^{-3} \varepsilon_g^3}{(1 - \varepsilon_g)^2}. \]  

(6.1)

6.1 Operating Conditions

The following operating conditions are used in the current simulation,

\[ T_{in} = 300 \text{ K}, \quad T_{wall} = 1273 \text{ K}, \quad u_{in} = 4.3566 \times 10^{-3} \text{ m/s}, \]

\[ \rho_{in} = 1.715 \times 10^{-2} \text{ kg/m}^3, \quad \mu_{in} = 1.1233 \times 10^{-5} \text{ N s/m}^2, \]

\[ Gr = 7.13 \times 10^4, \quad Re = 5.588, \quad Pr = 1.438, \]

\[ Da = 8.215 \times 10^{-3}, \quad Sc = 0.388. \]  

(6.2)

As can be noticed, we have selected reference values based on inlet conditions. These inlet conditions exist at the inlet of the pipe (not shown in Fig. 3.1) that supply the reactor with \( CH_4 \), where the velocity is assumed to be one-dimensional.

6.2 Chemical Kinetics and Deposition Rate

Since the gas-phase and surface reaction chemistry may include many reaction steps which result in a stiff system of equations with a large number of unknowns, we presently simulate this mechanism using a simple two-step reaction mechanism as in [50]:

\[ CH_4 \xrightarrow{k_1} \frac{1}{2}C_2H_2 + \frac{3}{2}H_2, \]  

(6.3)

\[ C_2H_2 + C(s) \xrightarrow{k_s} C(s) + 2C(b) + H_2. \]  

(6.4)
The first reaction (gas-phase) describes the decomposition of \( CH_4 \) into two components: acetylene, \( C_2H_2 \), and hydrogen, \( H_2 \). The second reaction step (surface reaction), which is necessary to predict the change in porosity of \((C/C')\) composites, describes the deposition of carbon inside the porous substrates. Based on [9], methane, acetylene, ethylene, benzene, and ethane are the major species that contribute in the carbon deposition, however in the present simulation we consider acetylene only. The reaction rate constant for the surface reaction is written in terms of a sticking (probability) coefficient. At the moment, due to lack of knowledge about \( k_1 \), we use an estimated value [225]. The reaction rate \( k_s \) is based on experimental data [9].

Rates of production of each species can be written explicitly as

\[
\dot{\omega}_{CH_4} = -\frac{\varepsilon_g k_1 \rho Y_{CH_4}}{\dot{\omega}_r}, \quad (6.5)
\]
\[
\dot{\omega}_{C_2H_2} = \frac{1}{2} \frac{\varepsilon_g k_1 M_{C_2H_2} \rho Y_{CH_4}}{\dot{\omega}_r M_{CH_4}} - k_s \lambda S_v \frac{\Gamma_s \rho Y_{C_2H_2}}{\dot{\omega}_r}, \quad (6.6)
\]
\[
\dot{\omega}_{H_2} = \frac{3}{2} \frac{\varepsilon_g k_1 \rho Y_{CH_4} M_{H_2}}{\dot{\omega}_r M_{CH_4}} + k_s \lambda S_v \frac{\Gamma_{tot} \rho Y_{C_2H_2} M_{H_2}}{\dot{\omega}_r M_{C_2H_2}}, \quad (6.7)
\]
\[
\dot{\omega}_s = 2 \lambda k_s S_v \frac{\Gamma_{tot} \rho Y_{C_2H_2} M_C}{\dot{\omega}_r M_{C_2H_2}}, \quad (6.8)
\]

where \( k_1 = 2.24 \times 10^{14} e^{-E_1/(RT)} \) with \( E_1 = 3.64 \times 10^5 \text{ J/mol} \) [225]. \( S_v \) is gas/solid surface area per unit volume of the porous media. The preforms used for CVI/CVD typically have a complex porous structure. However we can simulate the surface to volume ratio using a cylindrical pore model [230]:

\[
S_v(\varepsilon_g) = \frac{2 \sqrt{\varepsilon_{g_0}} \sqrt{\varepsilon_g}}{r_0}, \quad (6.9)
\]

where \( r_0 \) is the initial pore radius, \( \varepsilon_{g_0} \) is the initial concentration of \( \varepsilon_g \), and \( k_s \) is
the surface reaction rate that can be written as [83]

$$k_s = \left( \frac{\gamma_i}{1 - \gamma_i/2} \right) \frac{1}{(\Gamma_{tot})^m} \sqrt{\frac{RT^*}{2\pi M_i}}. \quad (6.10)$$

$$\frac{\gamma_i(\theta)}{\gamma_i(0)} = (1 - \theta)^n. \quad (6.11)$$

Here \( \Gamma_{tot} \) is the site density which is taken as \( 5.2683 \times 10^{-9} \) mol/cm\(^2\) [331], \( m \) is the sum of all the surface reactants’ stoichiometric coefficients, \( n \) is the number of sites needed to hold the adsorbate, \( \gamma_{C_2H_2} = 3.5 \times 10^{-5} \) at pressure 20 torr [9], \( \gamma_i(0) \) is the sticking coefficient at zero coverage \( \theta \). There are many models that represent the sticking factor as a function of coverage. The simplest, the Langmuir, model suggests a decrease of sticking coefficient with increasing coverage as in Eqn. (6.11). For \( n = 1 \) the sticking factor decrease linearly. The coverage depends on the partial pressure of the species. Hence, as the pressure increases, the number of active sites decrease due to increased coverage and hence the surface reaction decreases. This is consistent with the observation of Bammidipati et al. [50] who noted a decrease in the sticking coefficient whenever pressure increased.

6.3 Results

The simulation is initiated by using the steady state solution with initial porosity \( \varepsilon_{g0} = 0.71 \) and proceed to integrate the equations until the dimensionless time of \( t = 2 \times 10^5 \).

The reaction rate, and hence the deposition rate, is sensitive to temperature, therefore it is important to first examine the temperature field within the reactor as well within the porous substrates. This is displayed in Fig. 6.1(a).

As can be seen, the gas temperature near the reactor wall is higher than
that in the middle of the reactor. Although temperature variation appears to be small, this small variation has a great impact on the porosity change within the substrates, as shown in Fig. 6.1(b). The magnitude of the velocity field inside the reactor, including within the porous substrates, at the final time is shown in Fig. 6.1(c).

Figs. 6.2(a), 6.2(b), and 6.2(c) show the methane, acetylene, and hydrogen mass fraction distributions inside the reactor at the final time. It is clear that the maximum amount of acetylene exists at the first disk brake, this is consistent with Fig. 6.1(b) where the first disk has the lowest porosity at the final time.

Moreover, Figs. 6.3 and 6.4 elucidate how the porosity varies, at different times overall and in the midsection of the 1st brake from the bottom of the reactor.

There appears to be an upward flow next to the reactor wall and a downward flow in the middle of the reactor. Moreover it is clear that the magnitude of velocity decreases with time within substrates due to the decreasing porosity. This decrease appears to affect the complete velocity distribution within the reactor.

Clear recirculation regions are apparent in the preheat zone and in the middle of the reactor. From Fig. 6.5 we can see how the vertical velocity component varies with time at a cross-section passing through the middle of brake 11 from the bottom.

To summarize, in this chapter we have implemented successfully the low Mach number equations within the reactor and substrates. We have accounted for the reaction within the substrates by using a two step reaction mechanism for methane decomposition which subsequently gave rise to a variation in porosity with time within them. We observe that the reaction rate is very sensitive to temperature and it greatly affects the deposition rate. Lastly, we note that to improve the
Figure 6.1: Variables at final time.
Figure 6.2: Variables at final time.
Figure 6.3. Variation of porosity at the midpoint of the 1st brake from the bottom as a function of time.

Figure 6.4. Porosity distribution at the midsection of the 1st brake from the bottom at different times.
Figure 6.5. Vertical velocity component through a cross-section passing through the midpoint of brake 11 from the bottom.

uniformity of temperature and deposition rate within substrates the flow field has to be modified.
CHAPTER 7
TRANSIENT SOLUTION OF THE CHEMICAL VAPOR DEPOSITION/INFILTRATION REACTOR

In this chapter we present the transient solution of the CVI/CVD reactor using equations specified in Sec. 3.2, the stiff gas-phase reaction mechanism in Table 3.8, the surface reaction mechanism in Table 3.11, and model \textsuperscript{#2} for surface to volume ratio from Table 3.6. We set the pyrolytic carbon density to be 2000 $kg/m^3$, fiber density to be 1600 $kg/m^3$ and initial carbon fiber radius of 5$\mu m$.

The results are presented through a parametric study where we specify temperatures of 1273 $K$, 1323 $K$, 1373 $K$, and 1423 $K$, and pressures of 10 $torr$, 20 $torr$, 40 $torr$, and 60 $torr$. Hence, we present 16 different cases. All simulations are performed at the constant mass flow rate of 6.23 $m^3/hr$ (220 $ft^3/hr$) at 300 $K$ by changing the inlet parabolic velocity distribution at the inlet accordingly. We attempted to obtain results for the temperature of 1473 $K$ and pressures of 10 $torr$, 20 $torr$, 40 $torr$, and 60 $torr$. Nevertheless we could not get convergence for initial quasi state solution for these results.

We believe that the quasi-steady state solution is the most important solution that should be examined carefully. In fact one should be able to predict porosity variations by examining this solution. There are many figures associated with this parametric study, some of the results vary from one case to the other, while some do not change that much. However, for completeness we have included them for
reference. We discuss only the most important results from the quasi-steady state
solution of the 16 cases, followed by presenting the porosity variation with time
for each of these cases. It is important to note that each figure has its own color
bar scale. Finally the initial average carbon deposition rates are summarized as
function pressure and temperature at different brakes.

7.1 Results of Initial Quasi-Steady State Solution

Figs. 7.2, 7.3, 7.4, and 7.5 represent temperature distributions within the
brakes for cases. Fig. 7.1 shows temperature distribution at temperature of 1373 \( K \)
and pressure of 20 \( \text{torr} \) for a temperature range of 1372 – 1373 \( K \). In this simu-
lation we have not accounted for radiation. However, the brakes are maintained
in a uniform temperature that is near the reactor wall temperature. This is very
similar for all other cases. For that reason the radiation heat flux is not considered
in coming results.

Figs. 7.6, 7.7, 7.8, and 7.9 represent the kinetic energy distributions (based
on Darcian velocity within brakes, \( U_D = \varepsilon_g u_g \)) within the reactor as well as
within the brakes. As shown, in all cases the velocity is high at the middle of
the reactor, while it is very small in the region between reactor walls and brakes.
This is has a tremendous effect of varying the species residence time within the
reactor and hence on the species concentrations as will be clear later. It is possible
that if baffles were used, this problem could be reduced. In addition, we find that
initially the velocity within the brakes is two orders of magnitude smaller than the
velocity in the region between the reactor wall and the brakes, and it decreases with
increasing porosity (as expected). Moreover the kinetic energy within the reactor
does not change that much with pressure, however it increases by increasing the

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Figure 7.1. Dimensional temperature distribution within brakes at $T = 1373$ K and $p = 20$ torr.
temperature.

Figs. 7.10, 7.11, 7.12, and 7.13 represent streamlines within the reactor. It can be noticed that recirculation region increases at the inlet by increasing the pressure. This could be eliminated by using baffles since it may result in a uniform temperature distribution at the inlet.

Figs. 7.14, 7.15, 7.16, and 7.17 represent the methane mass fraction distributions inside the reactor. It is very clear that methane experiences larger decomposition by increasing temperature or pressure. In addition methane experiences a very small decomposition for temperatures of 1273 K and 1323 K. Therefore we expect a very small deposition rates at these temperatures.

Figs. 7.18, 7.19, 7.20, and 7.21 represent hydrogen mass fraction distributions inside the reactor. As expected, the mass fraction increases by increases temperature or pressure. It should be noted that the hydrogen mass fraction in the brakes near the top is larger than in those near the bottom. This makes it very difficult to have a uniform deposition for all the stacked brakes.

Figs. 7.22, 7.23, 7.24, and 7.25 represent acetylene mass fraction distributions inside the reactor. Again, the mass fraction increases by increasing temperature or pressure. However, the mass fraction in the region between the reactor walls and brakes, are higher than in the middle of the reactor. This causes the deposition rate to be higher near the outer surface of the brakes than near the inner surface, since acetylene is the main depositing species and species least affected by hydrogen inhibition. This leads to pores being closed on the outer surface. The high acetylene concentration near reactor wall is due to the large residence time in this region, as can be seen from Figs. 7.6, 7.7, 7.8, and 7.9.

Figs. 7.26, 7.27, 7.28, and 7.29 represent ethylene mass fraction distributions
insider the reactor. Again, the mass fraction increases by increasing temperature or pressure. Acetylene is not affected much by the residence time as can be seen from the figures.

Figs. 7.30, 7.31, 7.32, and 7.33 represent benzene mass fraction distributions insider the reactor. Again, the mass fraction increases by increasing temperature or pressure. Benzene experiences the same phenomenon as acetylene, where concentrations within the region near the wall are higher than in the middle of the reactor. This is very clear when pressure increases.

Figs. 7.34, 7.35, 7.36, and 7.37 represent the ratio between acetylene concentration to benzene concentration. This ratio affects the texture of pyrolytic carbon deposited, as noted by Libermann and Pierson [106, 107]. The higher this ratio the heavier the pyrolytic carbon deposited is. This ratio decreases as flow moves towards the reactor exit. This is because acetylene reaches its peak early at the first brakes and start to decay with residence time. On the other hand benzene increases with residence time and decreases with increasing pressure at all temperatures. However at constant pressure, this ratio decreases with increasing temperature then start increasing again. It is clear that the heaviest pyrolytic structure can be achieved at the lowest temperature and pressure. However the deposition rate is extremely low at these conditions as will be shown later. The pyrocarbon textures does not depend only on $[C_2H_n] / [C_6H_m]$ but also on $[H_2] / [C_xH_y]$ as shown in [5, 67]. The higher this ratio is the lower the deposition rate is, due to the hydrogen inhibition effect as illustrated in Fig. 3.6. Therefore it is important to examine these ratios.

Figs. 7.38, 7.39, 7.40, and 7.41 represent the ratio between hydrogen concentration to acetylene concentration. It can be seen that at low temperatures the
rate of evolution of acetylene is larger than its counterpart of hydrogen and vice versa at high temperatures. It is very obvious that this ratio reaches its maximum at the largest temperature. In addition at this temperature there is a large disparity between the minimum and maximum value of the ratio. This predicts a large nonuniform porosity variation within brakes. The minimum value of this ratio falls within temperatures of $1323\, K$ and $1373\, K$. This non-uniformity is a result of the nonuniform distribution of $C_2H_2$ as will be shown later.

Figs. 7.42, 7.43, 7.44, and 7.45 represent the ratio between hydrogen concentration to ethylene concentration. This ratio increases by increasing temperature or pressure and is the only ratio that has uniform distribution within each brake.

Figs. 7.46, 7.47, 7.48, and 7.49 represent the ratio between hydrogen concentration to benzene concentration. It is clear that this ratio decreases with increasing pressure. In addition, this minimum of this ratio is at near the temperature of $1373\, K$ for pressures of $10 - 40\, torr$. As mentioned in Sec. 2.3.1, hydrogen has its inhibition effect on PAHs. Therefore having such nonuniform distribution of this ratio predicts a nonuniform distribution in porosity. As will be shown later, the nonuniform distribution of this ratio is due to the nonuniform distribution of $C_6H_6$.

Figs. 7.50, 7.51, 7.52, and 7.53 shows the initial carbon deposition rate within brakes. A general behavior can be noted is that the outer surfaces of brakes experience higher deposition rate than the inner surfaces. The main reason for this is the variation of acetylene and benzene species concentrations as shown earlier.
7.2 Results of Transient Quasi-Steady State Solution

We noted that the fluid flow, temperature and species concentration fields experience minor change during the infiltration process. Therefore we present here the porosity variation at different infiltration times for each of the previous cases.

Figs. 7.54, 7.55, 7.56, 7.57, 7.58, 7.59, 7.60, and 7.61 show that at the low temperatures of 1273 $K$ or 1323 $K$ the deposition rate is very small at all pressures. In addition Figs. 7.62, 7.63, 7.66, and 7.67 show that at low pressure, 10 torr or 20 torr, the deposition rate is also very small even at high temperatures. Whereas on Fig. 7.64 the deposition rate is moderate and on Fig. 7.65 the deposition rate is higher. A higher deposition rate can be seen on Figs. 7.68 and 7.69 as well. Is should be noted that there is a large gradient in porosity between the outer surface an inner surface, especially at higher temperatures and pressures. In fact, it can be seen that, in all cases the inner brakes radii experience a very low deposition rate and hence high porosity. This is a result of acetylene and benzene species distribution within the reactor, as mentioned earlier.

It is worth noting that for the case of temperature 1373 $K$ and pressure of 60 torr we have been able to obtain porosity after 26 days only and not after 30 days as for other cases. This is because a very large gradient is constructed between the outer and inner radii of the brakes. In addition, we use model 2 from Table 3.6 where surface/volume ratio depends on logarithm of porosity. Therefore, the more we approach small porosity the more we approach singularity in surface/volume ratio. This is also true for tortuosities laws as mentioned in [3]. Similarly, we have been able to obtain porosity only after 24 days for the case with temperature of 1423 $K$ and pressure of 40 torr, and 11 days for the case
with temperature of 1423 K and pressure of 60 torr.

7.3 Initial Average Carbon Deposition Rates

From examining the numerous previous solution figures, it is difficult to find the optimum operating conditions. Therefore the following figures reveal clearly the optimum operating conditions. Figs. 7.3 show the initial average carbon deposition rates within each brake at different operating conditions as function of dimensionless brake locations.

It can be noticed that at temperatures of 1273 K or 1323 K, at any pressure level, the deposition rates are very small. In addition, there is a remarkable improvement in the deposition rate by changing the temperature from 1323 K to 1373 K whereas a weak improvement can be noticed by changing the temperature from 1373 K to 1423 K. This could be a result of breaking the carbon/hydrogen bond $C(H)$ near 1100 K as mentioned in Sec. 2.3.1. On the other hand at pressures of 40 torr or 60 torr and temperature of 1423 K, the pores on the outer brake surfaces are closed early as it is shown from Figs. 7.68, 7.69. A similar early pores closure can be seen from Fig. 7.65 at temperature of 1373 K and pressure 60 torr. That leaves us with temperature of 1373 K and pressure of 40 torr. These operating conditions are the optimum operating conditions for achieving reasonable uniform deposition rates along the reactor vertical heights. This conclusion is supported by Fig. 7.3 where the average carbon deposition rates, at temperature 1373 K and pressure 40 torr, for different infiltration times are still uniform along the reactor vertical height.
Figure 7.2: Dimensionless temperature field at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.3: Dimensionless temperature field at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.4: Dimensionless temperature field at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.5: Dimensionless temperature field at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.6: Dimensionless kinetic energy at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.7: Dimensionless kinetic energy at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.8: Dimensionless kinetic energy at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.9: Dimensionless kinetic energy at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.10: Streamlines at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.11: Streamlines at 20 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.12: Streamlines at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.13: Streamlines at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.14: $CH_4$ mass fraction at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.15: \( CH_4 \) mass fraction at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.16: $CH_4$ mass fraction at 40 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.17: $CH_4$ mass fraction at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.18: $H_2$ mass fraction at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.19: $H_2$ mass fraction at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.20: $H_2$ mass fraction at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.21: $H_2$ mass fraction at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.22: $C_2H_2$ mass fraction at 10 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.23: $C_2H_2$ mass fraction at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.24: $C_2H_2$ mass fraction at 40 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.25: $C_2H_2$ mass fraction at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.26: $C_2H_4$ mass fraction at 10 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.27: $C_2H_4$ mass fraction at 20 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.28: \( C_2H_4 \) mass fraction at 40 torr and 1273 \( K \), 1323 \( K \), 1373 \( K \), 1423 \( K \) (from left to right).
Figure 7.29: $C_2H_4$ mass fraction at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.30: $C_6H_6$ mass fraction at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.31: $C_6H_6$ mass fraction at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.32: $C_6H_6$ mass fraction at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.33: $C_6H_6$ mass fraction at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.34: \([C_2H_2] / [C_6H_6]\) at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.35: $[C_2H_2]/[C_6H_6]$ at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.36: $[C_2H_2] / [C_6H_6]$ at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.37: \([C_2H_2] / [C_6H_6]\) at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.38: \([H_2]/[C_2H_2]\) at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.39: $[H_2] / [C_2H_2]$ at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.40: \([H_2]/[C_2H_2]\) at 40 \(\text{torr}\) and 1273 \(K\), 1323 \(K\), 1373 \(K\), 1423 \(K\) (from left to right).
Figure 7.41: $[H_2] / [C_2H_2]$ at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.42: $[H_2]/[C_2H_4]$ at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.43: \([H_2]/[C_2H_4]\) at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.44: \([H_2]/[C_2H_4]\) at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.45: $[H_2] / [C_2H_4]$ at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.46: $[H_2]/[C_6H_6]$ at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.47: $[H_2] / [C_6H_6]$ at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.48: $[H_2] / [C_6H_6]$ at 40 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.49: $[H_2] / [C_6H_6]$ at 60 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.50: Carbon deposition rate $kg/m^3/sec$ at 10 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.51: Carbon deposition rate $kg/m^3/sec$ at 20 torr and 1273 K, 1323 K, 1373 K, 1423 K (from left to right).
Figure 7.52: Carbon deposition rate $kg/m^3/sec$ at 40 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.53: Carbon deposition rate $kg/m^3/sec$ at 60 torr and 1273 $K$, 1323 $K$, 1373 $K$, 1423 $K$ (from left to right).
Figure 7.54: Porosity distribution at 1273 K and 10 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.55: Porosity distribution at 1273 K and 20 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.56: Porosity distribution at 1273 K and 40 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.57: Porosity distribution at 1273 K and 60 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.58: Porosity distribution at 1323 $K$ and 10 $torr$ after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.59: Porosity distribution at 1323 K and 20 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.60: Porosity distribution at 1323 K and 40 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.61: Porosity distribution at 1323 K and 60 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.62: Porosity distribution at 1373 $K$ and 10 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.63: Porosity distribution at 1373 K and 20 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.64: Porosity distribution at 1373 $K$ and 40 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.65: Porosity distribution at 1373 K and 60 torr after 2, 8, 16, 24, and 26 days (from left to right).
Figure 7.66: Porosity distribution at 1423 K and 10 torr after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.67: Porosity distribution at 1423 \( K \) and 20 \( \text{torr} \) after 2, 8, 16, 24, and 30 days (from left to right).
Figure 7.68: Porosity distribution at 1423 \( K \) and 40 torr after 2, 8, 16, and 24 days (from left to right).
Figure 7.69: Porosity distribution at 1423 $K$ and 60 torr after 2, 8, and 11 days (from left to right).
Figure 7.70. Initial average carbon deposition rates at different pressures and temperatures.
Figure 7.71. Average carbon deposition rates at $T = 1373 \text{ K}$ and $p = 40 \text{ torr}$. 
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

We implement the low Mach number equations for reactive flow in porous media using an efficient proposed scheme that is second order in time and space. In addition an integration methodology is proposed for long time infiltration process. That includes implementation of Strang splitting operator to overcome temporal stiffness as well as fractional step method to overcome problem of solving large system of DAEs. For optimization purpose, this integration methodology is used to investigate the effect of varying pressure and temperature within the reactor through a parametric study.

Increases temperature causes deposition rates to increase too. However temperature has the same effect on all brakes since all brakes experience uniform temperature distribution. This is a result of having a very slow flow at the interface. Therefore there is enough time for heat to transfer from reactor walls to brakes by convection and diffusion before reaching the end of the preheat zone.

Uniform temperature distribution within brakes causes species concentrations to be responsible to porosity variations within brakes. However we find that there is a major difficulty in trying to optimize the reactor operating conditions due to many reasons. Large number of disk brakes as well as stacking them vertically
make it impossible to have all brakes experience the same deposition rate due to species variation throughout the reactor. In addition the acetylene as well as benzene experience large variation in the radial direction which causes large porosity gradient in that direction.

We also note that stacking the brakes on the top of each other almost cancel convection effect within the brakes which reduces deposition rate. In addition, the flow velocity as well as species concentrations in volumes between brakes are very small. This extremely reduces infiltration in the direction of the shortest infiltration length. Therefore, the brakes experience infiltration from one side only which is the outer surface in the direction of the longest length. This causes a crust to be formed on the outer surface causing closure of pores and hence stop infiltration process. That is obvious at cases of high temperatures and pressures. On the other hand, at low pressure of 10 \textit{torr} and 20 \textit{torr}, the deposition rates are very small at all temperatures, whereas at 60 \textit{torr}, the deposition rate is very high for temperatures of 1373 \textit{K} and 1423 \textit{K}. Therefore, we expect that the ideal infiltration conditions to fall between 20 – 40 \textit{torr} and temperature 1373 – 1423 \textit{K}.

By using the previously suggested operating conditions, a speed up as well as uniformity for the deposition process can be achieved in case we have uniform species concentrations across the radial direction. This could be achieved by using baffles at the reactor entrance that may reduce axial velocity at the center of the reactor. Hence, increases residence time at the center of reactor. This allows for methane to decompose in the same rate as in the region between brakes and reactor wall which reduces depositing species gradient in the radial direction. Therefore a uniform deposition rates can be achieved at the inner as well as outer radii of brakes.
Even though we may achieve a better species concentrations by increasing residence time, deposition rates may be reduced as a result of increasing hydrogen concentration. As an evidence to hydrogen effects on deposition rates, the outer surfaces of lower brakes experience lower porosity than outer surfaces of upper brakes event hough all brakes experience almost the same depositing species concentrations. This is mainly due to hydrogen species concentration which is higher at upper brakes than at lower brakes. Therefore hydrogen inhibition effect are higher at upper brakes especially for acetylene and benzene. Therefore residence time has to adjusted with operating conditions such that the ratios of $H_2/C_2H_2$, $H_2/C_2H_4$, and $H_2/C_6H_6$ are minimum. This is the case at a temperature of 1373 K and pressure of 20 – 40 torr. This support previous conclusion about the ideal operating conditions.

8.2 Recommendations

8.2.1 Recommendations for the Reactor

Optimization of the reactor first requires the achievement of initial uniform deposition rate within all brakes. Then transient solution can be examined at different infiltration times. In addition different flow rates should be considered. Therefore, the following can be suggested:

- In the case we want to achieve uniform deposition rate within the current reactor, temperature gradient in the vertical as well as radial directions should be used. We can use temperature that is higher at the inner brake surface than at the outer surface. In addition temperature at the upper brakes should be higher than that at lower brakes.
The hydrogen concentration plays an essential role in the rate as well as uniformity of deposition within brakes. Reducing hydrogen content will increase the deposition rate. However hydrogen could be important in achieving uniform deposition since it allows for species to infiltrate before they deposit. In the current reactor, the residence time is large which allows for large amount of hydrogen to be produced at the top of reactor. As a result we should expect brakes at the top of reactor to have lower deposition rate. Therefore we should try to reduce reactor length. This need some more investigation since we should allow for acetylene and benzene to be produced. There should be an optimum length at different operating conditions that allow for densification for a certain number of stacked brakes. In addition using a catalysis, within brakes, that absorb hydrogen can result in a higher densification rate.

The region between the reactor walls and brakes should be enhanced such that the residence time is not that large as in the current cases. That will help to achieve a better uniform acetylene as well as benzene concentrations across the radial direction of the reactor. In addition it will delay blocking of surface pores at early infiltration times. This should be examined in the existence of baffles at the entrance.

Diluent methane should be examined since methane with large mass fraction is being throughout at the exit of the reactor. As we mentioned earlier, carbon deposition can not be achieved directly from methane. However it can be achieved from methane products such as $\text{CH}_3$.

A substantial change in the reactor geometry could result in a fast and
uniform deposition rate within all brakes. All brakes should be exposed to same species concentrations. That can be achieved by putting all brakes on the same horizontal elevation. In addition infiltration should be achieved through largest surface area that is normal to smallest brake thickness. In other words brakes should be rotated $90^\circ$ around radial direction. That will help also to increase kinetic energy within brakes and hence increase species mass flux within brakes and deposition rate. This could also be achieved by increasing gap between brakes.

8.2.2 Recommendations for Different Models

Different models have been used in the reactor simulation. Due to lack of data, some of them may not be accurate. However the proposed integration methodology allows for testing different models. Some suggestions regards improving simulation results are:

- The effect of using multicomponent or Maxwell-Stefan diffusion coefficients instead of binary diffusion coefficients should be examined. In using binary diffusion within Fick’s law, we depend on using methane as the dominant species through the reactor. However, this may not be the case at high temperatures and pressures where large amount of methane is decomposed to other products. Hence, methane is not the dominant specie. This could result in an error in estimating the diffusion mass fluxes.

- The current gas-phase reaction mechanism is tested at low residence time. This is not the case in our reactor where large residence time exists. Hence an experimental results are need to test that reaction mechanism at long residence times. Same conclusion can be draw for surface reaction mechanism
which is not well understood. Therefore a well specified experiments are needed for validation of deposition model at different operating conditions. In addition inhibition functions at different temperatures and pressures are needed to be well defined and tested.

- Evolution of surface/volume ratio model during infiltration process is still ad-hoc. This ratio plays an important rule in the deposition model, however there are so many models with large variations exists. Therefore we should build this model for certain brake fibers with certain architecture using different experiments. A similar model is needed for permeability and tortuosities.

- The proposed integration procedure allows for using larger number of species and hence better reaction mechanism. In addition it allows for an efficient parallel computations to be implemented. Therefore, whenever possible, we should use a better gas-phase reaction mechanism.
APPENDIX A

LOW MACH NUMBER EQUATIONS FOR REACTIVE FLOW INSIDE POROUS MEDIUM

In this section we show how to obtain the governing equations in Sec. 3.2. In addition we show that mass, momentum, and energy are conserved within these equations. The general formulation of the multiphase mixture governing equations derived by Paolucci [332] are used. Constitutive equations are obtained by comparing previous governing equations with the governing equations for two-phase flow presented by Powers [221]. Finally the corresponding low Mach number equations are obtained by following the derivation given by Paolucci [127]. Note that in following analysis all variables are dimensional and should be starred. However in this appendix the star is dropped for simplicity.

A.1 Multiphase Mixture Governing Equations

A.1.1 Mass Balance

The evolution of mass of species $k$ is given by [332],

$$\frac{\partial (\varepsilon_k \rho_k)}{\partial t} + \nabla \cdot (\varepsilon_k \rho_k \mathbf{u}_k) = \dot{\omega}_k \tag{A.1}$$

where $\rho_k$ is the average mass density of species $k$, $\mathbf{u}_k$ is the velocity field of species $k$ relative to a fixed laboratory frame of reference, $\dot{\omega}_k$ is the production rate of
species $k$ with respect to the total volume, and $\varepsilon_k$ is the volume fraction of species $k$.

Summing Eqn. (A.1) over the number of gaseous species ($N_g$) we get,

$$\frac{\partial (\varepsilon_g \rho_g)}{\partial t} + \nabla \cdot (\varepsilon_g \rho_g \mathbf{u}_g) = \dot{\omega}_g$$  \hspace{1cm} (A.2)

whereas summing Eqn. (A.1) over the number of solid species ($N_s$) we get,

$$\frac{\partial (\varepsilon_s \rho_s)}{\partial t} + \nabla \cdot (\varepsilon_s \rho_s \mathbf{u}_s) = \dot{\omega}_s$$  \hspace{1cm} (A.3)

In case we have stagnant solid species ($u_s = 0$) and assuming ($\rho_s = \text{const}$), Eqn. (A.3) can be written as:

$$\frac{\partial \varepsilon_s}{\partial t} = \frac{\dot{\omega}_s}{\rho_s}$$  \hspace{1cm} (A.4)

It can be noted that the summation of Eqn. (A.2) and Eqn. (A.3) results in the conventional conservation of mass for the system,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$  \hspace{1cm} (A.5)

where,

$$\dot{\omega}_g + \dot{\omega}_s = 0,$$  \hspace{1cm} (A.6)

$$\varepsilon_g + \varepsilon_s = 1,$$  \hspace{1cm} (A.7)

$$\rho = \varepsilon_g \rho_g + \varepsilon_s \rho_s,$$  \hspace{1cm} (A.8)

$$\rho \mathbf{u} = \varepsilon_g \rho_g \mathbf{u}_g + \varepsilon_s \rho_s \mathbf{u}_s,$$  \hspace{1cm} (A.9)
\[ 
\varepsilon_g \rho_g = \sum_{k=1}^{N_g} \varepsilon_k \rho_k, \quad \text{(A.10)} \\
\varepsilon_s \rho_s = \sum_{l=1}^{N_s} \varepsilon_l \rho_l, \quad \text{(A.11)} \\
\varepsilon_g \rho_g \mathbf{u}_g = \sum_{k=1}^{N_g} \varepsilon_k \rho_k \mathbf{u}_k, \quad \text{(A.12)} \\
\varepsilon_s \rho_s \mathbf{u}_s = \sum_{k=1}^{N_s} \varepsilon_k \rho_k \mathbf{u}_k, \quad \text{(A.13)} \\
\dot{\omega}_g = \sum_{k=1}^{N_g} \dot{\omega}_k, \quad \text{(A.14)} \\
\dot{\omega}_s = \sum_{l=1}^{N_s} \dot{\omega}_l. \quad \text{(A.15)} 
\]

By using Eqn. (A.4) and Eqn. (A.6), Eqn. (A.2) can be written as:

\[
\varepsilon_g \frac{\partial \rho_g}{\partial t} + \nabla \cdot (\varepsilon_g \rho_g \mathbf{u}_g) = \left( \frac{\rho_g}{\rho_s} - 1 \right) \dot{\omega}_s. \quad \text{(A.16)}
\]

A.1.2 Mass Diffusion

The partial mass fraction of the gaseous species \( k \) can be defined as:

\[
Y_k = \frac{\varepsilon_k \rho_k}{\varepsilon_g \rho_g} \quad \text{(A.17)}
\]

Substituting Eqn. (A.17) into Eqn. (A.1) we get,

\[
\frac{\partial}{\partial t} (\varepsilon_g \rho_g Y_k) + \nabla \cdot (\varepsilon_g \rho_g \mathbf{u}_k Y_k) = \dot{\omega}_k \quad \text{(A.18)}
\]

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By introducing the mass average velocity of gaseous species $u_g$, we can write the mass diffusion velocity of gaseous species $k$ as:

$$ u^d_k = u_k - u_g \quad k = 1, \ldots, N_g $$  \hspace{1cm} (A.19)

By substituting Eqn. (A.19) in Eqn. (A.18) we get:

$$ \frac{\partial}{\partial t} (\varepsilon_g \rho_g Y_k) + \nabla \cdot (\varepsilon_g \rho_g u_g Y_k) = \dot{\omega}_k - \nabla \cdot (\varepsilon_g \rho_g u^d_k Y_k) $$  \hspace{1cm} (A.20)

By expanding the LHS of Eqn. (A.20) and using Eqn. (A.2) and Eqn. (A.6) we get:

$$ \rho_g \varepsilon_g \left( \frac{\partial Y_k}{\partial t} + u_g \cdot \nabla Y_k \right) = \dot{\omega}_k + Y_k \dot{\omega}_s - \nabla \cdot J^m_k $$  \hspace{1cm} (A.21)

where $J^m_k$ is the diffusion mass flux of species $k$ defined as:

$$ J^m_k = \varepsilon_g \rho_g Y_k u^d_k $$  \hspace{1cm} (A.22)

### A.1.3 Linear Momentum Balance

The evolution of linear momentum of species $k$ is given by [332],

$$ \frac{\partial}{\partial t} (\varepsilon_k \rho_k u_k) + \nabla \cdot (\varepsilon_k \rho_k u_k u_k) = \nabla \cdot (\varepsilon_k \sigma_k) + \varepsilon_k \rho_k g_k + F_k $$  \hspace{1cm} (A.23)

where $\sigma_k$ is the total stress tensor of species $k$, $g_k$ is the external body force per unit mass, and $F_k$ is the macroscale momentum source arising from the mass transfer rate and stress interactions between interfaces of species $k$ and other
species. Summing Eqn. (A.23) over gaseous species we get,

$$\frac{\partial}{\partial t} (\varepsilon_g \rho_g \mathbf{u}_g) + \nabla \cdot \sum_{k=1}^{N_g} (\varepsilon_k \rho_k \mathbf{u}_k \mathbf{u}_k) = \nabla \cdot \sum_{k=1}^{N_g} (\varepsilon_k \mathbf{\sigma}_k) + \varepsilon_g \rho_g g_g + F_g \quad (A.24)$$

where,

$$F_g = \sum_{k=1}^{N_g} F_k \quad (A.25)$$

$$\varepsilon_g \rho_g g_g = \sum_{k=1}^{N_g} \varepsilon_k \rho_k g_k \quad (A.26)$$

By using Eqn. (A.19) in Eqn. (A.24) we get:

$$\frac{\partial}{\partial t} (\varepsilon_g \rho_g \mathbf{u}_g) + \nabla \cdot \sum_{k=1}^{N_g} \varepsilon_k \rho_k \mathbf{u}_k (\mathbf{u}_g + \mathbf{u}_k^d) = \nabla \cdot \sum_{k=1}^{N_g} (\varepsilon_k \mathbf{\sigma}_k) + \varepsilon_g \rho_g g_g + F_g \quad (A.27)$$

Eqn. (A.27) can be simplified as:

$$\frac{\partial}{\partial t} (\varepsilon_g \rho_g \mathbf{u}_g) + \nabla \cdot (\varepsilon_g \rho_g \mathbf{u}_g \mathbf{u}_g) = \nabla \cdot (\varepsilon_g \mathbf{\sigma}_g) + \varepsilon_g \rho_g g_g + F_g \quad (A.28)$$

where,

$$\varepsilon_g \mathbf{\sigma}_g = \sum_{k=1}^{N_g} \varepsilon_k (\mathbf{\sigma}_k - \rho_k \mathbf{u}_k^d \mathbf{u}_k^d) \quad (A.29)$$

Similar results can be obtained by summing Eqn. (A.23) over solid species,

$$\frac{\partial}{\partial t} (\varepsilon_s \rho_s \mathbf{u}_s) + \nabla \cdot (\varepsilon_s \rho_s \mathbf{u}_s \mathbf{u}_s) = \nabla \cdot (\varepsilon_s \mathbf{\sigma}_s) + \varepsilon_s \rho_s g_s + F_s \quad (A.30)$$
where,

\[ \varepsilon_s \sigma_s = \sum_{k=1}^{N_s} \varepsilon_k \left( \sigma_k - \rho_k u_k^d u_k^d \right) \]  \hspace{1cm} (A.31)

\[ F_s = \sum_{k=1}^{N_s} F_k \]  \hspace{1cm} (A.32)

\[ \varepsilon_s \rho_s g_s = \sum_{k=1}^{N_s} \varepsilon_k \rho_k g_k \]  \hspace{1cm} (A.33)

It can be noted that the summation of Eqn. (A.28) and Eqn. (A.34) results in the conventional conservation of linear momentum for the system,

\[ \frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho uu) = \nabla \cdot \sigma + \rho g + F \]  \hspace{1cm} (A.34)

where,

\[ F = F_g + F_s \]  \hspace{1cm} (A.35)

\[ \rho g = \varepsilon_g \rho_g g_g + \varepsilon_s \rho_s g_s \]  \hspace{1cm} (A.36)

\[ \sigma = \varepsilon_g \left( \sigma_g - \rho_g u_g^d u_g^d \right) + \varepsilon_s \left( \sigma_s - \rho_s u_s^d u_s^d \right) \]  \hspace{1cm} (A.37)

where \( u_g^d \) and \( u_s^d \) are the relative velocities, with respect to the mixture velocity \( u \), of gas and solid respectively defined as,

\[ u_g^d = u_g - u, \]  \hspace{1cm} (A.38)

\[ u_s^d = u_s - u. \]  \hspace{1cm} (A.39)

Now we assume the the linear momentum source term is only due to interphase change between gas and solid mixtures. In other words \( F_g = -F_s \), hence, \( F = 0 \).
In our simulations we are concerned only with the linear momentum of the gas mixture Eqn. (A.28) since we take \( u_s = 0 \). A constitutive equation is still needed to express \( F_g \). By comparing Eqn. (A.28) with its counterpart presented by Powers [221], we find that \( F_g \) can be written as:

\[
F_g = p_g \nabla \varepsilon_s - \delta (u_s - u_g) - \frac{1}{2} (u_s + u_g) \omega_g
\]  

(A.40)

where \( \delta \) is an interphase drag parameter that can be interpreted as Darcy and Ergun terms [268]. In case of stagnant solid species (\( u_s = 0 \)) this term can be expressed as:

\[
\delta = \frac{\mu_g \varepsilon_g^2}{k} u_g + \frac{\varepsilon_g C_E |u_g|}{k^2} \varepsilon_g \rho_g u_g
\]  

(A.41)

by substituting Eqns. (A.2), (A.40), (A.41) in Eqn. (A.28) we get:

\[
\varepsilon_g \rho_g \left( \frac{\partial u_g}{\partial t} + (u_g \cdot \nabla) u_g \right) = -\varepsilon_g \nabla p_g + \nabla \cdot (\varepsilon_g \tau_g) + \varepsilon_g \rho_g g_g
\]

\[- \left( \frac{\nu_g}{k} + \frac{\varepsilon_g C_E |u_g|}{k^2} \right) \varepsilon_g \rho_g u_g + \frac{u_g}{2} \sum_{j=1}^{N_s} \dot{\omega}_j ; \]  

(A.42)

A.1.4 Energy Balance

The total energy of species \( k \) is given by [332],

\[
\frac{\partial}{\partial t} \left[ \varepsilon_k \rho_k \left( e_k + \frac{1}{2} u_k^2 \right) \right] + \nabla \cdot \left[ \varepsilon_k \rho_k \left( e_k + \frac{1}{2} u_k^2 \right) u_k \right] = -\nabla \cdot (\varepsilon_k q_k - \varepsilon_k \sigma_k \cdot u_k) \\
+ \varepsilon_k \rho_k \left( \varsigma_k + g_k \cdot u_k \right) + \Upsilon_k 
\]  

(A.43)

where \( e_k \) is the internal energy of species \( k \), \( q_k \) is the conductive heat flux of species \( k \), \( \varsigma_k \) is the external energy associated with species \( k \), and \( \Upsilon_k \) is the energy
source term associated with species $k$. The inner product of $\mathbf{u}_k$ and Eqn. (A.23) provides the kinetic energy equation of species $k$ (with the use of Eqn. (A.1)):

$$
\frac{\partial}{\partial t} \left( \varepsilon_k \rho_k \frac{1}{2} \mathbf{u}_k^2 \right) + \nabla \cdot \left( \varepsilon_k \rho_k \frac{1}{2} \mathbf{u}_k \mathbf{u}_k \right) = \mathbf{u}_k \cdot \nabla \cdot (\varepsilon_k \mathbf{\sigma}_k) + \varepsilon_k \rho_k \mathbf{u}_k \cdot \mathbf{g}_k
$$

$$
+ \left( \mathbf{F}_k \cdot \mathbf{u}_k - \dot{\omega}_k \frac{\mathbf{u}_k^2}{2} \right) \quad (A.44)
$$

Now subtracting Eqn. (A.44) from Eqn. (A.43), leaves us with the internal energy equation of species $k$:

$$
\frac{\partial}{\partial t} (\varepsilon_k \rho_k e_k) + \nabla \cdot (\varepsilon_k \rho_k e_k \mathbf{u}_k) = -\nabla \cdot (\varepsilon_k \mathbf{q}_k) + \varepsilon_k \mathbf{\sigma}_k : \nabla \mathbf{u}_k + \varepsilon_k \rho_k s_k +
$$

$$
\left[ \nabla \cdot \mathbf{u}_k + \dot{\omega}_k \frac{u_k^2}{2} - \mathbf{F}_k \cdot \mathbf{u}_k \right] \quad (A.45)
$$

By using Eqn. (A.1) in Eqn. (A.45) we get:

$$
\varepsilon_k \rho_k \frac{De_k}{Dt} = -\nabla \cdot (\varepsilon_k \mathbf{q}_k) + \varepsilon_k \mathbf{\sigma}_k : \nabla \mathbf{u}_k + \varepsilon_k \rho_k s_k +
$$

$$
\left[ \nabla \cdot \mathbf{u}_k + \dot{\omega}_k \left( e_k - \frac{u_k^2}{2} \right) - \mathbf{F}_k \cdot \mathbf{u}_k \right] \quad (A.46)
$$

where $De_k/Dt$ is the substantial derivative of the internal energy of species $k$. The internal energy of species $k$ is related to the enthalpy of formation of species $k$ by the following relation:

$$
e_k = h_k - \frac{p_k}{\rho_k} \quad (A.47)
$$

Therefore, by taking the substantial derivative of both sides of Eqn. (A.47) and by using Eqn. (A.1), we get:
\[
\frac{D\epsilon_k}{Dt} = \frac{Dh_k}{Dt} + \frac{p_k}{\varepsilon_k\rho_k}\dot{\omega}_k - \frac{p_k}{\rho_k}\nabla \cdot u_k - \frac{1}{\varepsilon_k\rho_k}\frac{D(\varepsilon_k p_k)}{Dt}
\] (A.48)

Now substituting Eqn. (A.48) and Eqn. (A.47) into Eqn. (A.46), we get:

\[
\varepsilon_k\rho_k\frac{Dh_k}{Dt} = \frac{D(\varepsilon_k p_k)}{Dt} - \nabla \cdot (\varepsilon_k \mathbf{q}_k) + \varepsilon_k \mathbf{\tau}_k : \nabla \mathbf{u}_k + \varepsilon_k \rho_k \varsigma_k + \left[ \gamma_k - \dot{\omega}_k (h_k - \frac{u_k^2}{2}) - \mathbf{F}_k \cdot \mathbf{u}_k \right]
\] (A.49)

where,

\[
\mathbf{\tau}_k = \mathbf{\sigma}_k + p_k \mathbf{I}
\] (A.50)

Now assuming that the gaseous species behave as ideal gases, the gas and solid are in thermal equilibrium, the conductive heat flux can be expressed by Fourier’s law, and external energy does not exist, these assumptions can be expressed as the following:

\[
dh_k = c_{pk}dT_k \quad \text{ideal gas}
\] (A.51)

\[
dT_1 = dT_2 = \cdots = dT \quad \text{local thermal equilibrium}
\] (A.52)

\[
\mathbf{q}_k = -k_k \nabla T \quad \text{Fourier’s law}
\] (A.53)

\[
\varsigma_k = 0.
\] (A.54)

Using the above assumptions, Eqn. (A.49) can be written as:
\[ \varepsilon_k \rho_k c_k \left( \frac{\partial T}{\partial t} + \mathbf{u}_k \cdot \nabla T \right) = \frac{D (\varepsilon_k p_k)}{Dt} + \nabla \cdot (\varepsilon_k k_k \nabla T) + \varepsilon_k \mathbf{\tau}_k : \nabla \mathbf{u}_k + \] 
\[ \left[ \mathbf{\gamma}_k - \dot{\omega}_k (h_k - \frac{u_k^2}{2}) - \mathbf{F}_k \cdot \mathbf{u}_k \right] \] (A.55)

Summing Eqn. (A.55) over the total number of species \( N \) assuming that solid species are stagnant \( (\mathbf{u}_s = 0) \) gives:

\[ \rho c_p \frac{\partial T}{\partial t} + \left( \sum_{k=1}^{N_g} \varepsilon_k \rho_k c_k \mathbf{u}_k \right) \cdot \nabla T = \frac{Dp}{Dt} + \nabla \cdot (k \nabla T) + \mathbf{\tau} : \nabla \mathbf{u} - \] 
\[ \sum_{k=1}^{N} \omega_k h_k + \sum_{k=1}^{N_g} \dot{\omega}_k \frac{u_k^2}{2} + (\mathbf{\gamma} - \mathbf{F} \cdot \mathbf{u}) \] (A.56)

where,

\[ p = \sum_{k=1}^{N} \varepsilon_k p_k, \] (A.57)
\[ \mathbf{\gamma} = \sum_{k=1}^{N} \varepsilon_k \mathbf{\gamma}_k, \] (A.58)
\[ \mathbf{F} \cdot \mathbf{u} = \sum_{k=1}^{N} \mathbf{F}_k \cdot \mathbf{u}_k, \] (A.59)
\[ \mathbf{\tau} = \mathbf{\sigma} + p \mathbf{I}, \] (A.60)
\[ \rho c_p = \sum_{k=1}^{N} \varepsilon_k \rho_k c_k, \] (A.61)
\[ k = \sum_{k=1}^{N} \varepsilon_k k_k. \] (A.62)

Assuming that the interphase-excess energy is only due to interphase change between solid and gas, in other words, \( \mathbf{\gamma}_g = -\mathbf{\gamma}_s \), hence, \( \mathbf{\gamma} = 0 \). In addition by
using Eqn. (A.19), Eqn. (A.56) can be written as:

\[ \frac{\partial T}{\partial t} + \varepsilon_g \rho_g c_{p_g} u_g \cdot \nabla T = \frac{Dp}{Dt} + \nabla \cdot (k \nabla T) - \left( \sum_{k=1}^{N_g} \varepsilon_k \rho_k c_{p_k} u_k^d \right) \cdot \nabla T + \tau : \nabla u - \sum_{k=1}^{N_g} \dot{\omega}_k h_k + \sum_{k=1}^{N_g} \dot{\omega}_k \frac{u_k^2}{2} \]  

(A.63)

Now substituting of Eqns. (A.22), (A.17) in Eqn. (A.63) we get:

\[ \frac{\partial T}{\partial t} + \varepsilon_g \rho_g c_{p_g} u_g \cdot \nabla T = \frac{Dp}{Dt} + \nabla \cdot (k \nabla T) - \sum_{k=1}^{N_g} \mathbf{J}_k^m c_{p_k} \cdot \nabla T + \tau : \nabla u - \sum_{k=1}^{N_g} \dot{\omega}_k h_k + \sum_{k=1}^{N_g} \dot{\omega}_k \frac{u_k^2}{2} \]  

(A.64)

where,

\[ \varepsilon_g \rho_g c_{p_g} = \sum_{k=1}^{N_g} \varepsilon_k \rho_k c_{p_k}. \]  

(A.65)

A.2 Low Mach Number Equations

By following the derivation given by Paolucci [127], the corresponding low Mach number equations of Eqns. (A.16), (A.21), (A.42), (A.64) can be obtained as:

\[ \varepsilon_g \frac{\partial \rho_g}{\partial t} + \nabla \cdot (\varepsilon_g \rho_g u_g) = \left( \frac{\rho_g}{\rho_s} - 1 \right) \dot{\omega}_s. \]  

(A.66)

\[ \rho_g \varepsilon_g \left( \frac{\partial Y_k}{\partial t} + u_g \cdot \nabla Y_k \right) = \dot{\omega}_k + Y_k \dot{\omega}_s - \nabla \cdot \mathbf{J}_k^m, \]  

(A.67)
\[
\varepsilon_g \rho_g \left( \frac{\partial \mathbf{u}_g}{\partial t} + (\mathbf{u}_g \cdot \nabla) \mathbf{u}_g \right) = -\varepsilon_g \nabla \Pi + \nabla \cdot (\varepsilon_g \mathbf{t}_g) + \varepsilon_g \rho_g \mathbf{g}_g,
\]

\[
- \left( \frac{\nu_g}{\kappa} + \frac{\varepsilon_g C_E |\mathbf{u}_g|}{\kappa^{\frac{1}{2}}} \right) \varepsilon_g^2 \rho_g \mathbf{u}_g + \frac{\mathbf{u}_g}{2} \sum_{j=1}^{N_g} \dot{\omega}_j, \tag{A.68}
\]

\[
\rho c_p \frac{\partial T}{\partial t} + \varepsilon_g \rho_g c_p_g \mathbf{u}_g \cdot \nabla T = \nabla \cdot (k \nabla T) - \sum_{k=1}^{N_g} \mathbf{J}^{\text{m}}_k c_{p_k} \cdot \nabla T,
\]

\[
- \sum_{k=1}^{N} \omega_k h_k \tag{A.69}
\]

where \( \Pi \) is the hydrodynamic/hydrostatic gas pressure. The above equations in conjunction with Eqn. (A.4) can be written in dimensionless form using Eqn. (3.21). Subsequently, the governing equations in Sec. 3.2 are obtained.


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