Heat and Mass Transfer Correlations for Steam Methane Reforming in Non-Adiabatic, Process-Intensified Catalytic Reactors

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HEAT AND MASS TRANSFER CORRELATIONS FOR STEAM METHANE
REFORMING IN NON-ADIABATIC, PROCESS-INTENSIFIED CATALYTIC
REACTORS

by

Adam S. Kimmel, B.S.Ch.E.

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science

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ABSTRACT

HEAT AND MASS TRANSFER CORRELATIONS FOR STEAM METHANE REFORMING IN NON-ADIABATIC, PROCESS-INTENSIFIED CATALYTIC REACTORS

Adam S. Kimmel, B.S.Ch.E.
Marquette University, 2011

Because of its high energy density, hydrogen is a desirable energy source for the achievement of a renewable energy landscape. Though production methods like thermolysis, electrolysis and biomass conversion, among others, are thought to be long term renewable solutions, catalytic steam methane reforming (SMR) is currently the predominant mechanism to produce hydrogen on an industrial scale. The highly endothermic, transport-limited reforming process has also been scaled down through process intensification to create efficient small-scale hydrogen-generating systems. One proposed geometry utilizes a catalytic finned cylinder that provides a manufacturable solution to enable high-efficiency heat exchange and SMR reaction. An accurate representation of the reactor performance characteristics is imperative to the design of small-scale systems.

The Nusselt and Sherwood numbers, the respective dimensionless temperature and concentration gradients, are commonly used to model the transport characteristics. Previous works have outlined the significance of modeling techniques that include radial diffusion to capture the bulk-phase diffusive resistance. However, prior studies have either over-simplified the transport to neglect diffusion in the bulk fluid or employed CFD to include the relevant effects. A considerable limitation of CFD-derived solutions is a high degree of computational intensity.

In the current study, local transport coefficients are determined for the SMR reaction in a catalytic microchannel. The 2-D cylindrical transport equations are simplified based on approximations from prior work to represent the channel geometry. The applied assumptions dramatically decrease the model’s computation time. A finite central-differencing scheme is implemented to solve the coupled transport equations with the reaction kinetics, and is solved through simultaneous matrix inversion. A kinetic model for SMR reactions is included as a model subroutine to describe the highly non-linear transport/kinetic interactions, while accounting for species adsorption/desorption to and from the catalyst. The transport model is compared to known solutions for the desired boundary conditions to validate the diffusive effects. The full model is validated against experimental data, and is able to reasonably predict the expected transport behavior and chemical kinetic interactions in the catalytic microchannel.
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Adam S. Kimmel, B.S.Ch.E.

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Arrhenius pre-exponential factor</td>
</tr>
<tr>
<td>$A_c$</td>
<td>flow channel cross-sectional area</td>
</tr>
<tr>
<td>$A_{surf}$</td>
<td>reactor tube surface area</td>
</tr>
<tr>
<td>$c$</td>
<td>molar density</td>
</tr>
<tr>
<td>$c_p$</td>
<td>species heat capacity</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>binary diffusivity between species $A$ and $B$</td>
</tr>
<tr>
<td>$D_{AB, film}$</td>
<td>binary diffusivity between species $A$ and $B$ at the film temperature</td>
</tr>
<tr>
<td>$d_h$</td>
<td>hydraulic diameter</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration</td>
</tr>
<tr>
<td>$G$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$G_{i,T}$</td>
<td>temperature-specific molar Gibbs function of specie $i$</td>
</tr>
<tr>
<td>$G_{i,T_0}$</td>
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<td>gas hourly space velocity</td>
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<td>$H_{i,T_0}$</td>
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<td>molar flux of species $A$</td>
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<td>thermal conductivity of specie $i$ at the film temperature</td>
</tr>
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<td>kinetic reaction rate constant of reaction $(rxn=SMR, WGS, or RM)$</td>
</tr>
<tr>
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<td>adsorption coefficient of specie $i$</td>
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<tr>
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<tr>
<td>$L$</td>
<td>total channel length</td>
</tr>
<tr>
<td>$M_i$</td>
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<tr>
<td>$m$</td>
<td>mass flow rate</td>
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<td>constant wall temperature boundary condition of parameter $N$</td>
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</tr>
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</tr>
<tr>
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<td>pressure</td>
</tr>
<tr>
<td>$P^o$</td>
<td>standard pressure</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$Q$</td>
<td>rate of heat flow</td>
</tr>
<tr>
<td>$q_{exh}$</td>
<td>heat flux due to external heat source</td>
</tr>
<tr>
<td>$q_{rxn}$</td>
<td>heat flux generation/consumption due to chemical reaction</td>
</tr>
<tr>
<td>$R$</td>
<td>total channel radius</td>
</tr>
</tbody>
</table>
Re_d  hydraulic diameter-based Reynold's number
R_u  universal gas constant
r  radial position/direction
r_{A,n}  rate (formation of species A, reaction n)
Re  Reynold's number
S_{i,T_0}  temperature-specific molar entropy of specie i at standard pressure
S:C  steam to carbon ratio
Sc  Schmidt number
Sh  Sherwood number
T  temperature
T_m  bulk (mean) fluid temperature
T_{wall}  wall temperature
V  volume
y_A  mole fraction of species A
z  axial position/direction

\Delta  change (in)
\Delta H_{rxn}  heat of reaction
\gamma  exponent on Gz^{-1} term in Sherwood correlation
\varepsilon_i  conversion of specie i
\eta  catalyst effectiveness
\mu  dynamic viscosity
\rho  total flow density
\rho_A  mass density of species A
\rho_{bed}  catalyst bed density
\rho_{A,wall}  mass density of species A at the wall
\rho_c  mass density of species A far from the wall
\nu  stoichiometric coefficient
\nu_z  axial velocity
\nu_{z,m}  mean axial velocity
\omega_A  mass fraction of species A
1. INTRODUCTION / BACKGROUND

1.1 Industrial Applications of Hydrogen

Hydrogen has been gaining favor as a suitable alternative to foreign oil as an energy source. Because of the many methods by which it can be produced domestically, including corn and switch grass derivatives, there has been an increasing interest in developing products that utilize hydrogen as the primary energy source. In the short term, coal, another domestic though non-renewable resource, can also be used to produce hydrogen, thereby reducing the immediate pressure to import overseas petroleum. Hydrogen’s high mass-specific lower-heating valued-based energy density of 120 MJ/kg makes it favorable for many applications, and it is a potential alternative to the current oil-based energy production methods in the stationary power and automotive sectors. Historically, hydrogen has been used in several common industrial processes, as well.

1.1.1 Common Industrial Uses

Hydrogen’s primary industrial uses have been in ammonia production and oil refining. Ammonia, which consumes half of the globally-produced hydrogen, is produced by reacting atmospheric nitrogen with hydrogen. It is used in fertilizer manufacturing, industrial refrigeration and industrial chemical manufacturing (Ogden, 2004). Ammonia is also used in cleaning and sanitizing applications.

Hydrogen is also used in the oil refining process, an application which accounts for about 35% of the global hydrogen consumption. It is used to upgrade viscous oil constituents
to produce gasoline and diesel fuel, and also aids in sulfur removal. Reformed hydrogen is also used to reduce other atmospheric pollutants, such as nitric oxides (NO\textsubscript{x}) and other hydrocarbon fuel emissions. Sulfur and other emissions constituents are targets of continued fuel standards tightening in the US and Europe. Both sulfur and NO\textsubscript{x} are key contributors to acid rain, which is extremely detrimental to the regional climate. Increased focus in sulfur and NO\textsubscript{x} reduction has increased the demand for hydrogen production (Ogden, 2004).

Other uses for hydrogen which drive demand for production include metallurgy, chemicals and pharmaceuticals, glass and ceramics, food and beverages and electronics.

1.1.2 Fuel Cells

A well-known technology for converting the hydrogen into electrical energy is the fuel cell. Fuel cells have been gaining popularity in recent years due to their zero-emission stack reaction, whereby hydrogen is reacted with oxygen in the presence of an electrolyte to produce electricity with pure water as the reaction byproduct. Because fuel cells convert the chemical energy provided by a fuel directly into electrical energy, they can be about twice as efficient as conventional technologies that rely on a combustion step to convert the chemical energy into thermal energy before the subsequent conversion step to electrical energy, losing about 70% of their initial energy content as heat. Fuel cells are up to 60% efficient in energy conversion (with the remaining 40% lost as heat), and combined heat and power systems can attain energy conversions of up to 90%. Modine’s industrial research for fuel cells suggests that the market size stationary power generation market in both small scale ~1 kW residential combined heat and power use and large-scale ~100 kW distributed power generation use has
the potential to reach $2.4B and $16.8B, respectively. The largest market sector is the automotive market, which has potential revenues of up to $252B.

1.2 Hydrogen Production Methods

There are several prominent industrial approaches to hydrogen production. Each contains a series of reactions that are closely coupled with either the consumption or production of heat, and uses a catalyst to drive the reactants toward the desired reaction products. Currently, more than 95% of over 45 million tonnes per year of globally-produced hydrogen comes from fossil fuels, with nearly half of that amount derived from natural gas (Ogden, 2004). Much of the catalyst development to date has subsequently been focused on methane reaction constituents. Three of the commonly-employed hydrogen production schemes are given below.

1.2.1 Steam Methane Reforming (SMR)

Steam methane reforming (SMR) and water-gas shift (WGS) reactions are equilibrium reactions, each with a reaction-specific temperature, pressure and composition-dependent equilibrium constant \( K_{eq} \). This term relates the reaction Gibbs energy to the species composition at a given pressure and temperature. For the general SMR reaction

\[
\nu_{CH_4} CH_4 + \nu_{H_2O} H_2O \rightleftharpoons \nu_{CO} CO + \nu_{H_2} H_2
\]
The extent of chemical equilibrium reactions ($\varepsilon$) is dependent on temperature, pressure and reactant composition. Changing any of these parameters will influence the Gibbs energy of reaction, shifting the equilibrium composition to a new minimum Gibbs energy toward either the forward or reverse reaction products.

Steam methane reforming (SMR) of natural gas (~95% methane, depending on geographic region) has been widely used in industry to produce hydrogen for large industrial processes such as chemical manufacturing and petroleum refining (DOE, 2004). Up to 75% efficient in lower-heating value energy conversion, its high fuel conversion rate makes it an attractive method hydrogen production, and it is relatively cost-effective in relation to other hydrogen-producing processes due to the availability and the highly-developed infrastructure that currently exists in the U.S. for transporting natural gas (DOE, 2004). The global SMR reaction (R1) and coupled water-gas shift reaction (R2) are listed below:

\[
\begin{align*}
\text{R1:} & \quad \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \\
\text{R2:} & \quad \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

A major benefit of SMR is that it is a mature technology, and has been implemented for large-scale hydrogen production (Larminie and Dicks, 2003). Through Le Chatelier’s Principle, the desired reaction products favor low pressure conditions, thereby reducing
parasitic power requirements. Also, SMR produces more moles of hydrogen per mole of methane than other practiced reaction schemes. It is scaleable, and the reaction products can be tightly controlled through the selection of catalyst and operating temperature based on the principles of chemical equilibrium, which are discussed in section 1.3.2.1.

There are also several key challenges to steam methane reforming, however. Though it is an environmental improvement over gasoline combustion, the SMR and water-gas shift (WGS) reactions produce about two and a half times the amount of carbon dioxide as hydrogen on a mass basis. CO$_2$ is an undesirable greenhouse gas, and existing technologies to implement CO$_2$ reduction are largely untested (DOE, 2004). Furthermore, there are economic constraints on the steam methane reforming reaction. Because the primary fuel is natural gas, a fossil fuel, increased use of this technology would increase demand, and subsequently price, of natural gas. Equilibrium constraints limit the conversion of the methane, and at present it is still more expensive to produce an energy-equivalent quantity of hydrogen than it is to refine oil to produce gasoline. It is thus imperative to implement new reaction catalysts and process improvements to drive down the cost of hydrogen production from natural gas in order to reach the current DOE targets of $1.50/kg H_2$ and 75% reaction efficiency. A challenge to the implementation of hydrogen to the huge transportation sector is that, due to its low volumetric energy, a large volume of hydrogen is needed in the fuel tank compared to a thermally equivalent volume of gasoline.

Hydrogen production provides an environmental benefit due to its high mass-based lower heating value (LHV) energy density of 120 MJ/kg. For comparison, the LHV energy density of methane is 50.0 MJ/kg and that of gasoline is 44.3 MJ/kg (Heywood, 1988). The market sizes and DOE targets continue to push research and development toward a short-
term solution to introduce hydrogen into the economy, with steam methane reforming of natural gas providing a viable near-term path forward.

1.2.2 Catalytic Partial Oxidation (CPOX)

Methane can be converted to hydrogen through partial oxidation at 800-900°C by the use of a precious metal or nickel catalyst, or at higher temperatures without a catalyst. The global reaction is given below (Larminie and Dicks, 2003):

$$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad (R3)$$

A key benefit of CPOX is that it does not require steam, which greatly simplifies the system. This is significant in applications where the importance of primary component and balance-of-plant simplicity outweighs that of high electrical conversion efficiency targets. CPOX may also operate at a lower temperature range than SMR. When compared to the SMR process, CPOX produces 1 fewer mole of hydrogen per mole of methane, yielding lower CPOX system efficiencies than SMR systems. Another decrease in efficiency relative to SMR arises due to the exothermic nature of the reaction, as no heat from the energy conversion reaction can be utilized by the CPOX reaction (Larminie and Dicks, 2003).

CPOX applications have historically used air as the oxidizing agent, which dilutes the partial pressure of hydrogen due to the presence of nitrogen. This is especially detrimental to lower heating value-based efficiencies as the oxidizing agent (oxygen) comprises only 21 mol% per mole of air, leading to increased air flow requirements to supply the appropriate amount of oxygen.
1.2.3 Autothermal Reforming (ATR)

Hydrogen can also be produced by autothermal reforming (ATR). This is a process by which both steam and an oxidizer are combined with a fuel and fed to the fuel processor, and is a combination of SMR and CPOX. The major premise of ATR is that the combination of the two reaction types creates an essentially thermally neutral reaction environment, as shown from the combination of equations R1 and R3, shown below:

\[
\begin{align*}
CH_4 + H_2O & \rightleftharpoons CO + 3H_2 & (R1) \\
CH_4 + \frac{1}{2}O_2 & \rightarrow CO + 2H_2 & (R3)
\end{align*}
\]

This is a significant benefit, as no complex thermal management solution is required, greatly simplifying the design (Larminie and Dicks, 2003). Also, less steam is required than conventional reforming. Challenges include inherent decreased lower heating value-based system efficiencies from CPOX reaction inclusion, decreased levels of control due to differences in the reaction mechanisms at various points in the reactor and complicated, expensive catalyst application methods and materials due to the need to promote both parts of the reaction at different points along the reactor.

1.2.4 SMR and ATR Comparison

Both SMR and ATR can be shown to have advantages, and typically the two must be directly compared to determine suitability for a given system. For the current work, achieving desired methane conversion to hydrogen, low parasitic power consumption and thermal efficiency are critical. In addition to the characteristics listed above, Le Chatelier’s
Principle dictates that low pressure SMR yields more hydrogen than both high pressure SMR and ATR. Therefore, for this study, low pressure SMR (~1.1 bara) has been selected for the reaction scheme.

1.3 Catalytic Reactor Design

1.3.1 Reactor Type and Design Approaches

There are numerous reactor types that have been historically used in industry. The appropriate reactor for a given application is very much dependent on the reaction conditions, temperatures, required size, pressure drop requirements and cost targets. Two primary reactor types that have been used for applications similar to the current work include packed bed reactors and catalytic monolith reactors. They are discussed below along with their design approaches.

1.3.1.1 Packed Bed Reactor

The packed bed reactor (PBR) is essentially a plug-flow reactor with a solid packing material. A schematic of the PBR is shown in Figure 1.1.
The packed bed is a robust configuration that can be used for several purposes, including catalytic reactor, distillation column and a scrubber to improve air quality. A primary benefit of this type of reaction vessel is improved contact between dissimilar phases in a process (Fogler, 1999). For heterogeneous catalytic reaction, this characteristic is desirable. As a result, the PBR is one of the most common vessels for catalytic reaction, as the packing material for a reactor can be the reaction catalyst. The reaction catalyst for the SMR reaction is a high-cost precious metal, such as rhodium, palladium or platinum, so the PBR provides a higher conversion-per-unit mass of catalyst, which is highly desirable from a financial perspective (Froment and Bischoff, 1990). Also, manufacturing of the PBR is simple, as a standard tube can be used with the properly-sized catalyst section dropped in. Another benefit of the PBR with regard to its use as a reaction vessel is continuous operation, which is desirable for fuel cell applications as steady-state operation improves the efficiency and life span of the system components.

However, for the current application of coupling a reaction surface with heat transfer area, the packed bed may not be the most efficient choice. Key challenges to the PBR and its use for the work in this thesis are lack of temperature control, which is of prime concern with
the highly-endothermic SMR reaction, and maintaining the desired reactor volume to ensure conversion (Fogler, 1999). Due to a lack of temperature control, the reaction temperature may spike at some operating point, causing the catalyst substrate to sinter around the catalyst site, and decrease the amount of catalyst available for reaction. This may also hinder the flow distribution through the catalyst layer, potentially driving the flow through a smaller section of the catalyst and decreasing the catalyst life. Furthermore, because the reaction rate of the PBR is dependent on the mass of solid catalyst rather than the reactor volume, determining the correct amount of catalyst needed based on the reactor’s Gas-Hourly Space Velocity (GHSV), which is the volumetric flow rate of reactants divided by the reactor volume, becomes difficult. The GHSV is the typical metric provided by the catalyst supplier to the heat transfer component supplier to determine the required catalyst area needed on the reactor.

1.3.1.2 Catalytic Monolith

The catalytic monolith reactor has been gaining favor as a preferred reaction vessel over the last forty years due to its availability in various cross-sectional geometries, including circular, square, hexagonal, triangular and sinusoidal. The monolith reactor consists of a network of uniformly-arranged parallel channels. A schematic of an annular monolith is shown in Figure 1.2.
The channels are typically coated with a 10-200 µm porous layer called a washcoat, which contains catalyst supports, stabilizers and promoters (Bhattacharya, Harold and Balakotaiah, 2004b). The washcoat is primarily comprised of a high surface area inorganic oxide carrier, such as aluminum oxide or cerium dioxide, and is impregnated with precious metal salts. The monolith is then dipped into the washcoat slurry, and after a suitable weight gain has been achieved due to catalyst acquisition, the reactor is calcined at 400-500°C to improve the slurry bond to the reactor channel and to decompose the salts (Heck, Gulati and Farrauto, 2001). Reactors are sometimes pre-oxidized to ensure good adhesion between the monolith and the washcoat. These precious metal catalyst particles provide the reaction sites, and reaction may then occur when the reactants are diffused into the washcoat and reach the catalyst sites.

Its low pressure drop, high specific external surface area and improved transport properties make the catalytic monolith reactor an attractive candidate for a variety of industrial applications. These processes include emission control and oxidation of volatile organic compounds (West, Balakotaiah and Jovonovic, 2003). Catalytic monoliths are also
used for selective catalytic reduction of NO\textsubscript{x}, where low pressure drop is required, for
catalytic partial oxidation reactions (CPOX) and for liquid-phase hydrogenations. In
addition, these reactors also experience less precious metal catalyst attrition compared to that
of packed bed reactors (Bhattacharya et al., 2004b). The monolith has also been shown to
increase the catalyst effectiveness factor (which handicaps the reaction rate due to reactor
construction inefficiencies). This improvement represents a major advantage due to the
extremely high and increasing costs of the precious metals used to host the reactions (Heck et
al., 2001).

The continuing pressure to reduce emissions has led the catalytic monolith to be used
in catalytic combustion of methane, catalytic oxidation, hydrogenation or dehydrogenation of
aromatics, hydrogen generation for fuel cells and steam reforming of light hydrocarbons and
methanol (Bhattacharya et al., 2004b). Another relevant application of the catalytic monolith
reactor is its use as a multiphase reactor, which is intended to replace the packed bed and
batch reactors, such as continuous stirred tank reactor (CSTR) (Bhattacharya et al., 2004a).
Beyond the applications listed above, monoliths have also been used for three-way catalysts,
which simultaneously convert CO, HC’s and NO\textsubscript{x} to CO\textsubscript{2}, H\textsubscript{2}O and N\textsubscript{2} for automotive
exhaust clean-up. They have also been implemented for diesel oxidation catalysts,
preferential oxidation, aircraft ozone abatement, natural gas engines, ozone destruction in
automotive radiators and small engines, such as motorcycles, lawnmowers and chain saws.
Some research is being conducted to determine the applicability of the catalytic monolith
reactor to hydrogen peroxide production, nitric acid production, gas generation, and the
conversions of both alkanes and paraffins to olefins (Bhattacharya et al., 2004a).
While many of these applications are still in the research and development phase, the use of catalytic monoliths for emission control has enabled some prior experience to be gleaned, in order to better define a successful path forward. Additional analysis is needed in the areas of monolith preparation, reaction kinetics and heat transfer and reactor design simulation before clear industrial solutions can be defined.

The monolith also has several other advantages beyond those listed above. It eliminates internal, homogeneous diffusion limitations when thin reactor walls are implemented and decreases axial dispersion and back-mixing, leading to high selectivity of the reaction products. In addition, monolith reactors reduce fouling and plugging, which extends the lifetime of the catalyst. The monolith geometry also facilitates cleaning of particulates that have accumulated on the channel walls. Finally, one of the most significant advantages regarding the monolith reactor is that it lends itself to be able to be scaled up to larger sizes (Heck et al., 2001). This would enable small-scale prototypes to be realistic models of the performance of larger, more costly production designs. There is a substantial benefit in reducing the size of prototype reactors. In addition to being more economical to produce, smaller units can be built faster and require less space for performance testing. The overall significance of these advantages on the reaction efficiency is dependent on the specific reaction(s), and the respective reaction rates.

Monolith reactors are not without their challenges, however. They have the potential for reduced radial heat transfer, which inhibits temperature control for thin-wall ceramic monolith supports. Also, the opportunity for non-uniform flow distribution exists in the monolith geometry due to the quantity of small, thin-walled channels (Heck et al., 2001). Maldistribution is a major concern for these reactors, as this effect could lead to large,
undesirable gradients in temperature and concentration, possibly resulting in respective localized areas of decreased temperature and decreased or increased steam-to-carbon ratio. The long microchannel finned reactor design mitigates the potential for maldistribution, decreasing the risk. Due to the high sensitivity of the reaction kinetics on temperature, areas of low temperature may experience decreased conversion. If the steam-to-carbon ratio were too low, carbon may slip through the reactor, decreasing conversion and increasing the potential for coking downstream of the reactor should the temperature reach the necessary level. For an excessive steam-to-carbon ratio, the reaction does not have adequate chemical energy, and is therefore wasting some of the steam which is not being used to react with the hydrocarbon fuel. All three of these instances lead to depleted reactor effectiveness and decreased fuel conversion. Temperature gradients may also lead to mechanical fatigue or coking, as well. This study utilizes the monolith configuration as a model for a more complex configuration that is employed in the process-intensified reactor described in section 1.4.

1.3.2 Reaction Mechanisms and Kinetics

The SMR and WGS reactions are dependent on temperature, as stated above, and also on reaction kinetics. Due to the highly endothermic nature of the SMR reaction, supplying heat to the reaction has a direct and substantial impact on the conversion and reaction rate. Two factors determine the rate of reaction: the rate of species transport to and from the
reactor wall, and the reaction kinetics at the catalyst surface. The kinetics for a given
reaction $\nu_A A + \nu_B B \xrightarrow{k_f} \nu_C C + \nu_D D$ can be described by the Law of Mass Action:

$$\frac{d[A]}{dt} = -k_f [A]^\nu_A [B]^\nu_B + k_r [C]^\nu_C [D]^\nu_D$$  \hspace{1cm} (1.3)

where $k$ is the reaction rate constant, usually of the modified Arrhenius form

$$k = T^n A e^{\frac{-E_a}{R_u T}}$$  \hspace{1cm} (1.4)

In the above rate constant equation, $n$ defines the order of the direct temperature
multiplier, $T$ is the reaction temperature, $A$ is the pre-exponential coefficient, $E_a$ is the
activation energy required for the forward reaction, and $R_u$ is the universal gas constant.
Often, the temperature exponent $n$ in the Arrhenius equation is equal to 0.

A detailed kinetic mechanism which describes the elementary steps for methane
reforming over a nickel catalyst (Hecht et al., 2005) is presented in Table 1.1 as an example
of the many steps undertaken during the global conversion of methane to hydrogen, as
described in (R1) and (R2). The reaction steps are of the form of equation 1.3. $A$ is given in
terms of moles, cm and s and $E$ is in kJ/mol. Superscript $b$ denotes a sticking coefficient, and
subscript $c$ denotes coverage-dependent activation energy with total available surface site
density of $\Gamma=2.60 \times 10^{-9}$ mol/cm$^2$. The (s) term denotes an adsorbed species on the catalyst site.
Table 1.1: Heterogeneous reaction mechanism for methane reforming on Nickel-based catalysts (Hecht et al., 2005)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A'$(mol,cm,s)</th>
<th>n</th>
<th>$E_r$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $H_2$+Ni(s)+Ni(s)→H(s)+H(s)</td>
<td>1.000E-02$^a$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2 $H_2$(s)+H(s)→Ni(s)+Ni(s)+H$_2$</td>
<td>5.593E+19</td>
<td>0.0</td>
<td>88.12</td>
</tr>
<tr>
<td>3 O$_2$+Ni(s)+O(s)→O(s)+O(s)</td>
<td>1.000E-02$^b$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>4 O(s)+O(s)→Ni(s)+Ni(s)+O$_2$</td>
<td>2.508E+23</td>
<td>0.0</td>
<td>470.39</td>
</tr>
<tr>
<td>5 CH$_4$+Ni(s)→CH$_4$(s)</td>
<td>8.000E-03$^b$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>6 CH$_4$(s)→Ni(s)+CH$_4$</td>
<td>5.302E+15</td>
<td>0.0</td>
<td>33.15</td>
</tr>
<tr>
<td>7 H$_2$O+Ni(s)→H$_2$O(s)</td>
<td>1.000E-02$^b$</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>8 H$_2$O(s)→Ni(s)+H$_2$O</td>
<td>4.579E+12</td>
<td>0.0</td>
<td>62.68</td>
</tr>
<tr>
<td>9 CO+Ni(s)→CO(s)</td>
<td>8.000E-03</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>10 CO(s)→Ni(s)+CO</td>
<td>5.302E+15</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>11 O(s)+H(s)→OH(s)+Ni(s)</td>
<td>5.000E+22</td>
<td>0.0</td>
<td>97.90</td>
</tr>
<tr>
<td>12 O(s)+CO(s)→CO$_2$(s)+Ni(s)</td>
<td>2.000E+19</td>
<td>0.0</td>
<td>123.60</td>
</tr>
<tr>
<td>13 CO$_2$+Ni(s)→CO$_2$(s)</td>
<td>1.000E-05</td>
<td>0.0</td>
<td>123.60</td>
</tr>
<tr>
<td>14 O(s)+H$_2$O(s)→OH(s)+H$_2$O</td>
<td>3.000E+21</td>
<td>0.0</td>
<td>91.36</td>
</tr>
<tr>
<td>15 OH(s)+Ni(s)→O(s)+H$_2$O</td>
<td>1.000E-02$^b$</td>
<td>0.0</td>
<td>62.68</td>
</tr>
<tr>
<td>16 OH(s)+H$_2$O→O(s)+H$_2$O</td>
<td>3.000E+21</td>
<td>0.0</td>
<td>100.00</td>
</tr>
<tr>
<td>17 OH(s)+OH→O$_2$(s)+H$_2$O</td>
<td>5.423E+23</td>
<td>0.0</td>
<td>209.37</td>
</tr>
<tr>
<td>18 OH(s)+OH→O$_2$(s)+H$_2$O</td>
<td>3.000E+21</td>
<td>0.0</td>
<td>100.00</td>
</tr>
<tr>
<td>19 O(s)+H$_2$O→OH(s)+H$_2$O</td>
<td>4.579E+12</td>
<td>0.0</td>
<td>62.68</td>
</tr>
<tr>
<td>20 O(s)+CO→CO$_2$(s)+Ni(s)</td>
<td>1.418E+22</td>
<td>-3.0</td>
<td>115.97</td>
</tr>
<tr>
<td>21 CO$_2$+Ni(s)→CO$_2$(s)+Ni(s)</td>
<td>3.214E+23</td>
<td>-1.0</td>
<td>86.50</td>
</tr>
<tr>
<td>22 CO$_2$(s)+Ni(s)→CO(s)+H$_2$O</td>
<td>3.700E+21</td>
<td>0.0</td>
<td>127.98</td>
</tr>
<tr>
<td>23 HCO(s)+Ni(s)→CO(s)+H(s)</td>
<td>3.700E+24</td>
<td>-1.0</td>
<td>127.98</td>
</tr>
<tr>
<td>24 CO(s)+H(s)→HCO(s)+Ni(s)</td>
<td>2.333E+24</td>
<td>-1.0</td>
<td>95.80</td>
</tr>
<tr>
<td>25 CO(s)+Ni(s)→O(s)+CH(s)</td>
<td>7.914E+20</td>
<td>0.0</td>
<td>114.22</td>
</tr>
<tr>
<td>26 CH$_3$(s)+Ni(s)→CH$_3$(s)+H(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>57.70</td>
</tr>
<tr>
<td>27 CH$_3$(s)+Ni(s)→CH$_3$(s)+H(s)</td>
<td>4.438E+22</td>
<td>0.0</td>
<td>58.83</td>
</tr>
<tr>
<td>28 CH$_3$(s)+Ni(s)→CH$_3$(s)+H(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>100.00</td>
</tr>
<tr>
<td>29 CH$_3$(s)+Ni(s)→CH$_3$(s)+H(s)</td>
<td>9.513E+22</td>
<td>0.0</td>
<td>52.58</td>
</tr>
<tr>
<td>30 CH$_2$(s)+H$_2$→CH$_3$(s)+Ni(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>97.10</td>
</tr>
<tr>
<td>31 CH$_2$(s)+Ni(s)→CH$_2$(s)+H(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>97.10</td>
</tr>
<tr>
<td>32 CH$_2$(s)+H$_2$→CH$_2$(s)+Ni(s)</td>
<td>3.000E+24</td>
<td>0.0</td>
<td>76.43</td>
</tr>
<tr>
<td>33 CH$_2$(s)+Ni(s)→CH$_2$(s)+H(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>18.80</td>
</tr>
<tr>
<td>34 C(s)+H$_2$→CH(s)+Ni(s)</td>
<td>4.400E+22</td>
<td>0.0</td>
<td>160.49</td>
</tr>
<tr>
<td>35 O(s)+CH$_4$(s)→CH$_3$(s)+OH(s)</td>
<td>1.700E+24</td>
<td>0.0</td>
<td>88.30</td>
</tr>
<tr>
<td>36 CH$_4$(s)+OH→O(s)+CH$_3$(s)</td>
<td>8.178E+22</td>
<td>0.0</td>
<td>28.72</td>
</tr>
<tr>
<td>37 O(s)+CH$_3$(s)→CH$_2$(s)+OH(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>130.10</td>
</tr>
<tr>
<td>38 CH$_3$(s)+OH→O(s)+CH$_2$(s)</td>
<td>3.815E+21</td>
<td>0.0</td>
<td>21.97</td>
</tr>
<tr>
<td>39 CH$_3$(s)+OH→O(s)+CH$_2$(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>127.98</td>
</tr>
<tr>
<td>40 CH$_3$(s)+OH→O(s)+CH$_2$(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>127.98</td>
</tr>
<tr>
<td>41 CH$_2$(s)+H$_2$→CH$_3$(s)+Ni(s)</td>
<td>3.700E+24</td>
<td>0.0</td>
<td>52.58</td>
</tr>
<tr>
<td>42 C(s)+OH→O(s)+CH(s)</td>
<td>1.764E+21</td>
<td>0.0</td>
<td>129.08</td>
</tr>
</tbody>
</table>

Table 1.1: Heterogeneous reaction mechanism for methane reforming on Nickel-based catalysts (Hecht et al., 2005)
Catalysis targets the activation energy term in the rate constant equation. A catalyst, embedded into a washcoat covering the reaction surface, provides a lower-activation energy reaction path to achieve the desired product composition at lower temperatures. For a given set of inlet conditions and composition, different catalysts (usually nickel or precious metals such as rhodium, platinum or palladium) facilitate different reaction paths. The catalyst is selected to encourage the reaction to proceed toward the desired path. Figure 1.3, which shows the energy path of an exothermic reaction such as the water-gas shift reaction, illustrates the impact of a catalyst on chemical reactions (endothermic reactions would have a higher product enthalpy than that of the reactants).

![Impact of a catalyst on exothermic chemical reactions](image)

**Figure 1.3:** Impact of a catalyst on exothermic chemical reactions (Heck and Farrauto, 2002).

Lower activation energy defines the preferred reaction path; by lowering the overall activation energy, catalysts increase the reactant preference to the preferred reaction path in
the overall mechanism. The typical catalyst materials for SMR reactions are comprised primarily of rhodium with traces of platinum and/or palladium, where the objective is high-temperature reaction (e.g. 600-800°C) to yield the desired products hydrogen and carbon monoxide (Froment and Bischoff, 1990).

The rate constant equation (1.4) outlines the clear direct relationship between reaction kinetics and temperature. As a result, the kinetics suffer at lower operating temperatures, and the characteristic time scale for the reaction kinetics is high. For conventional monoliths, the higher transport rates lead to an almost uniform distribution of temperature/concentration in the channel (Bhattacharya et al., 2004a). This regime is termed “kinetically controlled [or kinetically limited],” as the efficiency of the reaction is dependent on how quickly the reaction can proceed at the lower operating temperature with the uniform temperatures/concentrations. Increasing temperature past a condition-specific value drives the reaction from a kinetically-limited reaction to a transport-limited reaction. In the transport-limited case, the rate at which species are transported to and from the reactor wall limits the efficiency of reaction. The relationship between kinetically-controlled reaction conditions and transport-controlled reaction conditions is often described by the Damköhler number. This parameter is defined by the following equation, comparing respective time scales for the species transport and the reaction kinetics:

$$Da = \frac{\tau_{\text{flow}}}{\tau_{\text{reaction}}}$$

(1.5)

For low Damköhler numbers the reaction is said to be kinetically limited, while for high Damköhler numbers the reaction is said to be transport limited.
1.3.2.1 Chemical Equilibrium

Chemical equilibrium is defined as a thermodynamically-specific composition at which the forward and reverse reaction rates are equal, where product compositions no longer change with time for a given temperature and pressure. The equilibrium state is determined by the Second Law of Thermodynamics for specified conditions. Equilibrium-limited reactions are reversible, whereas traditional mechanical engineering reactions, like combustion, are to a large degree irreversible. The reasoning for this can be found in the differential relation between Gibbs energy and its variables, temperature and pressure, is given as:

$$dG = VdP - SdT + \sum_{i=1}^{N} \mu_i dn_i$$  \hspace{1cm} (1.6)

The final term, $\mu_i$, is defined as the chemical potential, and is related to Gibbs energy by $\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{P,T,n_j}$, where all mole numbers are held constant except the $i^{th}$ (Smith, Van Ness and Abbott, 2001). So, equilibrium can be defined as the condition of zero chemical potential or minimum Gibbs free energy. For ideal gas mixtures, the Gibbs energy is expressed as:

$$\mu_{LT} \equiv \bar{G}_{LT} = G_{LT}^o + R_a T \ln \left( \frac{P_1}{P^o} \right)$$  \hspace{1cm} (1.7)

The Gibbs energy is expressed as the sum of the mole-weighted partial Gibbs energies of the individual species. The $G_{LT}^o$ term is the Gibbs energy of formation at standard pressure. For each species $i$ in a reacting mixture, the Gibbs of formation is given as (Smith et al., 2001):
\[ G_{i,T}^o = H_{i,T}^o - TS_{i,T}^o - \sum_j \nu_j (H_{j,T}^o - TS_{j,T}^o) \] (1.8)

The Gibbs energy of formation includes the formation energies of the elemental constituents \(j\) comprising species \(i\). For example, for the reaction \(C + 2H_2 \rightarrow CH_4\),

\[ G_{CH_4}^o = H_{CH_4}^o - TS_{CH_4}^o - \left[ \nu_C (H_C^o - TS_C^o) + \nu_H (H_H^o - TS_H^o) \right] \]

From equation (1.6) and the Second Law, it is observed that at both constant pressure and temperature, and no change in chemical potential (\(d\mu\)), the equilibrium composition of a reaction occurs at \((dG)_{P,T} = 0\). As a result, the state of chemical equilibrium is achieved by minimizing the Gibbs energy.

If a system were not at equilibrium, any spontaneous reaction that occurs at a constant temperature and pressure must decrease the total amount of system Gibbs energy (Smith et al., 2001). This trend is seen in Figure 1.4, where the Gibbs energy is plotted against the reaction coordinate \(\varepsilon\). The reaction coordinate is simply a measure of the extent of the reaction (and subsequently the appropriate species compositions) of a reaction at a constant \(T\) and \(P\). Therefore, the amount of Gibbs energy can be determined by \(\varepsilon\). The arrows indicate the directions of changes in Gibbs energy due to reaction.
In practice, for the type of reactor modeled in this study, the fluid composition should reach its equilibrium compositions after about half of the tube length. The reactor length is generally oversized to ensure the desired conversion is achieved.

1.4 Modine Catalytic Finned Cylinder Reactor

Conventional packed-bed and monolith reactor configurations are beneficial for numerous common industrial applications. For smaller-scale applications, there is an opportunity to increase the functionality of the reactor-containing component to integrate several functions in the reaction scheme. Modine Manufacturing Company has developed a
proprietary reactor design for use in fuel processing applications for fuel cell systems. The Modine reactor design is most similar to the catalytic monolith in its minichannel design (200µm<d_h<3mm), but with heat transfer in close proximity to the catalyst-coated surfaces.

The annular reactor design contains two baffle cylinders surrounding an inner cylinder with serpentine fins brazed to both sides to facilitate heat transfer. One of the fins contains a catalyst-containing washcoat to encourage the desired reaction products. A schematic of this reactor design is shown in Figure 1.5. The arrows represent flow direction, with the blue arrow illustrating the reacting flow and the red arrow representing the heat source – heated air with humidity and CO₂, due to catalytic combustion of fuel cell anode and cathode exhaust streams.

Figure 1.5: Modine catalytic finned cylinder reactor
There are numerous benefits of this reactor style. For the SMR reaction, the implementation of fins as a reactor surface provides compact extended surface area for the transport of the significant heat that is required for the reaction, which is difficult to accomplish in conventional monolith reactor designs. The heat source is located on the non-reactor side of the cylinder. The cylindrical design provides space on the interior of the cylinder for other system components, such as steam generators or combustors. The thermally unconstrained annular design reduces fatigue paths from large temperature gradients in the dissimilar reactor component materials. Industrial reactors employ constrained designs, increasing the probability of fatigue issues in high-temperature gradient conditions (DOE, 2004). As a result, the reactor can easily accept dissimilar flow rates on the heat source and reaction side.

A challenge of this type of reactor is in the attachment of the fin to the tube; if there are areas of unbrazed fin, the heat will not reach the reaction, which will reduce conversion to hydrogen, the primary reaction product. Another challenge with all micro- and minichannel reactors is in the application of the washcoat to the channels. Though the reaction surface fins are very accessible, the coating must be applied uniformly to provide the desired CH₄ conversion to H₂ and CO at the reactor’s gas hourly space velocity (GHSV – the ratio of volumetric flow to reactor volume). This operational parameter is constrained by the reaction kinetics and catalyst type to ensure sufficient residence time is provided to achieve the desired conversion, assuming that there is sufficient catalyst in the reaction area. In the transport-limited regime, it is critical to achieve sufficient transport of reacting species to and product species from the catalyst surface.
1.5 Transport Coefficient Derivation Methods

In the design of this type of process-intensified reactor it is necessary to develop accurate representations of transport characteristics for numerical models. Many reactor models utilize empirical correlations to approximate the heat and mass transfer. The correlations are generally derived from data for specific cases, geometry and reaction conditions. For example, the Nusselt number for laminar flow in a rectangular duct can be determined by:

\[ \text{Nu} = 8.235 \times (1 - 2.0421 \times a + 3.0853 \times a^2 - 2.4765 \times a^3 + 1.0578 \times a^4 - 0.1861 \times a^5) \]

where \( a \) is the channel aspect ratio (Kakaç, Shah and Aung, 1987).

When developing a new geometry and/or reaction scheme, the transport coefficients are usually approximated using the most applicable of the empirical correlations. For heat transfer in fully-developed laminar flow of constant properties (viscosity-driven flow conditions), the transport coefficient is constant; many correlations therefore implement a Reynolds and Prandtl-independent equation, which is a function of a geometric parameter, such as aspect ratio. For the case of heat-transfer coupled with wall reaction, the importance of the heat and mass transport on the flow characteristics is magnified, potentially leading to variations in the transport coefficients in either absolute constant value or slope of coefficient curve along reactor.

Reactions at the channel wall impose concentration and/or temperature gradients in the transverse direction, normal to the flow. The treatment (or negligence) of these gradients has historically limited the accuracy and robustness of transport coefficient correlations.
(Hayes and Kolaczkowski, 1999). Many correlations do not define the local transport coefficients, but only provide an overall approximation of the transport over the entire reaction/heat transfer surface length.

Previous work, which has focused on the external transport in gas-solid systems, has utilized simplified heat and mass transfer boundary conditions and broad assumptions to represent the transport behavior. These simplifications have reduced the accuracy of the prior studies. Due to its strong dependence on temperature, the rate of the SMR reaction is limited by either the rate of heat supplied to the reaction or by the reaction kinetics. Many prior works have neglected diffusion in the direction normal to the wall, which could limit the accuracy of the predicted results. The Nusselt and Sherwood numbers, the respective dimensionless temperature and concentration gradients, describe the transport characteristics of a given geometry by providing a comparative ratio of convection to diffusion. These parameters can be used to characterize the transport for catalytic reactor design. An accurate model of the local transport properties could lead to substantial improvements in predicting the performance of a catalytic reactor, which requires significant time and cost investments to manufacture at both the prototype and the production levels.

1.5.1 Definition of Transport Coefficients

The respective definitions of the mass and heat transfer coefficients are shown below, as are the definitions of the dimensionless concentration and temperature gradients, Sherwood and Nusselt number (Incropera and Dewitt, 2002). The transport equations for the desired geometry are solved to obtain the concentration and temperature difference terms,
and the diffusion properties $D_{AB}$ and $k$ are temperature-dependent and determined at the film temperature, the arithmetic mean of the bulk fluid and wall surface temperatures. The hydraulic diameter, $d_h$, is given by the desired tube geometry.

$$h = \frac{k_{wall}}{T_{wall} - T_m} \left. \frac{\partial T}{\partial r} \right|_{r=R}$$

$$h_{mass,A} = \frac{D_{A,wall}}{\rho_{A,wall} - \rho_{A,m}} \left. \frac{\partial \rho_A}{\partial T} \right|_{r=R}$$

$$Sh_A = \frac{h_{mass,A} d_h}{D_{A,film}} = Sh_A(z, Re, Sc)$$

$$Nu = \frac{h d_h}{k_{film}} = Nu(z, Re, Pr)$$

### 1.6 Thesis Objectives and Manuscript Summary

The objective of this research is to extend prior correlation derivation approaches for similar and familiar geometries to derive local mass and heat transfer coefficients for steam methane reforming in a catalytic finned cylinder with an external heat source. The boundary layer approximations to the Navier-Stokes equation have been validated for other reaction mechanisms with good agreement to experimental data (Raja, Kee, Deutschmann, Warantz and Schmidt, 2000), and will be applied to the SMR reaction. The 2-D model assumptions and boundary conditions of this study are taken mainly from the 1999 Hayes and Kolaczkowski study, and the reactor inlet flow and composition is taken from a current industrial application of the geometry. The formulation will also include an external heat source supplied at the wall and will implement the Xu and Froment LHHW mechanism for
the SMR reaction. The model will account for radial diffusion, which has not been done in the literature for SMR reactions.

In the following chapters, a detailed review of the historical transport coefficient approach methodologies will be given, the model details and solution methodology will be described and the analysis will be applied to round-tube geometry. The transport and kinetics will be solved simultaneously for temperature and concentration using a commercially available software package. The temperature and concentration gradients are used to derive the heat and mass transfer coefficients, which can be directly used to derive the Nusselt and Sherwood numbers to model the respective heat and mass transport in the channel, including radial diffusion effects. Conclusions and recommendations will be given.
2. STATE OF THE ART IN TRANSPORT COEFFICIENT FORMULATION

In order to extend the prior work on catalytic monolith transport coefficient formulation, it is necessary to define the state of the art. Nusselt and Sherwood number, which are the dimensionless temperature and concentration gradients, are used to approximate the respective energy and mass transport. The detailed derivation of these parameters, which are generally defined in equation 1.10, is given in Chapter 3. As stated, to obtain the correlations the transport equations must first be solved for temperature and concentration.

To accurately characterize the present state of the research, prior models, assumptions and approaches must be investigated. A common initial assumption, also used in the current work, is to approximate the reactor matrix with a single channel, assuming uniform distribution within the reactor, so that each channel sees the same flow rate (Raja, Kee, Deutschmann, Warantz and Schmidt, 2000). Most prior works have assumed no interaction between the channel and the ambient environment, something this study aims to include due to the unique configuration of the Modine geometry which hosts the reaction on extended heat transfer surface. With the single channel assumption, the transport can be mathematically represented by a coupled convection-diffusion equation in the fluid phase, where the species within the fluid are brought to the wall, and a diffusion-reaction equation within the washcoat of the channel (Bhattacharya, Harold and Balakotaiah, 2004b). A schematic of the studied geometry is shown in Figure 2.1.
An effectiveness factor, $\eta$, has been historically used to approximate the washcoat diffusion, allowing a de-coupling of the two processes described above. These assumptions gave rise to two primary approaches: a 1-D two-phase model, developed by Ablow and Wise in 1979 and extended by Bensalem and Ernst in 1982, and a 2-D convection-diffusion model with wall reaction, first presented by Damköhler in 1937 and later extended by Heck et al. in 1976 and Lee and Aris in 1977. These approaches are reviewed in the following two subsections.
2.1 1-D Two-Phase Analytical Approach

One-dimensional, two-phase models have been derived by averaging the full model over a cross-section of the channel, and are computationally efficient. The two phases are a solid phase (catalyst) and a gaseous phase (fluid). The transport coefficients link the mass and heat transfer between the wall and the bulk fluid, and include an effectiveness factor to approximate both the diffusion into and the reaction within the washcoat (Bhattacharya, Harold and Balakotaiah, 2004b). The assumptions include smooth, right-cylinder geometry, steady-state, ideal gas, azimuthal symmetry, negligible homogeneous reaction, radiation and gravity and negligible axial diffusion, as the axial convective transport is assumed to be much larger than diffusion in the axial direction, infinitely fast radial diffusion (no \( r \) dependence). The general equations for the 1-D model are given in equations 2.1-4, with \( z \) as the axial direction.

**Continuity:**

\[
\frac{\partial}{\partial z} \left( \rho v_z \right) = 0 \tag{2.1}
\]

**Momentum conservation:**

\[
\left( \rho v_z \frac{\partial v_z}{\partial z} \right) = - \frac{\partial P}{\partial z} + \left( \mu \frac{\partial^2 v_z}{\partial z^2} \right) \tag{2.2}
\]

**Energy conservation:**

\[
\left( \rho c_p v_z \frac{\partial T}{\partial z} \right) = \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) \tag{2.3}
\]
Species conservation:

\[
\left( \rho D_z \frac{\partial \omega_A}{\partial Z} \right) = \frac{\partial}{\partial z} \left( \rho D_A \frac{\partial \omega_A}{\partial Z} \right)
\]  

(2.4)

The initial study, presented in 1979 by Ablow and Wise, investigated the catalytic combustion reaction of propylene and hydrogen. This application of catalytic monolith reactors experienced increased attention at that time due to its ability to facilitate heterogeneous reactions at temperatures low enough to inhibit formation of nitric oxides and other pollutants over a wide range of equivalence ratios, which are undesired byproducts of high-temperature combustion reactions. The Ablow and Wise analysis included both heterogeneous reaction at the tube wall and homogeneous reactions in the gas phase. The heterogeneous reactions were the species reacting on the channel wall, and the gas-phase homogeneous reactions were thought to increase the degree of reactant conversion because the catalytic monolith was mass transfer limited in the authors’ study. Prior work had described computational studies, which included numerical models of temperature-dependent transport and kinetic parameters. Computation time was found to be a significant challenge of these methods, so Ablow and Wise developed a simplified, theoretical model to characterize the reaction and transport characteristics. This model was compared to experimental data of various fuels in tubular reactors.

Having neither data nor a sufficient reaction mechanism, the authors assumed first order reaction rate in fuel and zero order reaction rate in oxygen concentration. The kinetics were broadly approximated by global Arrhenius-type reaction rates from previously-existing studies. Adiabatic channel conditions were assumed. Further assumptions in the Ablow and
Wise model included steady state and heat transfer terms representing convection in the gas, conduction to the surroundings of channels along the periphery of the monolith and axial conduction in the tube wall near the entrance region where temperature and concentration gradients are the highest. After neglecting axial conduction, two analytical results were found: a diffusion-limited solution and a transport-limited one.

The authors listed a primary discrepancy between the 1-D model and the experimental data to be the omission of axial heat transfer along the duct wall near the entry region of the tube. The study also found that homogeneous reaction did not have significant effect under their conditions. The authors’ results compared favorably to the experimental data presented. The model did not, however, adequately represent the behavior at the duct inlet at which the account for radial diffusion is most significant for performance predictions.

Bensalem and Ernst extended the Ablow and Wise study to homogeneous-heterogeneous carbon monoxide combustion in catalytic monoliths in 1982. This theoretical study investigated a two-section reactor, which is shown to perform better than the Ablow and Wise model. A schematic of the author’s reactor is shown in Figure 2.2.
Though it consumes less catalyst, this reactor style was developed to have higher reactor efficiency than the constant cross-section design, and it also has reduced pressure drop. Relevant model assumptions include: steady state, adiabatic reactor, negligible axial and radial diffusion, both hetero- and homogeneous reactions, constant temperature wall boundary condition, uniform catalyst distribution along the channel axis and negligible internal diffusion.

The homogeneous reaction kinetics were patterned after a model by Sobolev in 1958, which approximates the reaction as first order in CO and zeroth order in $O_2$, and includes a first order relation with the mole fraction of CO in the pre-exponential term. Voltz (1973) provided the kinetic model for the heterogeneous reaction. The assumption of negligible coating thickness yielded a catalyst effectiveness factor of 1. The effectiveness factor would reduce the amount of heat and mass transfer generation by including diffusive effects through the catalyst coating layer. It should be noted that the heterogeneous kinetic model developed
by Voltz was taken from data over a temperature range of 477-644K. However, since the reaction experiences decreased dependence on kinetics at temperatures exceeding about 900K in favor of diffusion/transport limited-behavior, the authors stated that the model of the catalytic rate equation had no effect on the solution.

The major outcome of this study was that in the two-chamber reactor, only the inlet is transport-limited. The kinetic dependence increases with the proportional increase of the temperature-dependent reaction rate. Also, in the range of 650-1100K, both hetero- and homogeneous reactions were found to be significant. Later works, including Hayes and Kolaczkowski in 1994 and Deutschmann and Schmidt in 1998, supported Ablow’s and Wise’s conclusion that for pressures below 1 bar, homogeneous reactions may be neglected.

Another significant outcome of the Bensalem and Ernst study was the conclusion that catalytic monolith reactors are robust enough to support varying operating conditions. The two-stage reactor presented in the Bensalem and Ernst study is designed to maximize efficiency and conversion in the smaller diameter, mass transfer-controlled inlet region. A pre-exponential factor used to approximate diffusion in the bulk phase in the 1-D model, was assumed to be 1 in the initial condition for both the kinetically-controlled and mass transfer-controlled regimes. The approximation led to over-predictions in the Sherwood number.

A 2003 study by West, Balakotaiah and Jovanovic investigated the first normalized Fourier weight and its significance in the mass transfer-controlled regime in detail, as the diffusive terms more accurately predicted the transport behavior in the entire reactor. The authors found, through both experimental and theoretical investigations, that the value should be about 0.8 for most channel geometries. Fully-developed flow was assumed, L/d of around
60 to eliminate axial diffusion, and negligible diffusion through the washcoat. Also, a high wall temperature (530-700K) was assumed to eliminate reactant concentration at the wall due to infinitely fast reaction. Finally, a less common assumption was made: that the inlet concentration was low enough to neglect the temperature dependence of velocity and diffusivity.

The model derived in the West study yielded a variance from the experimental solution of a maximum of 10%. Physical property variations were thought to negatively affect the exit conversion in the mass transfer-controlled regime. Using the first normalized Fourier weight can improve the predictability of the 1-D two-phase model while being able to neglect radial diffusion. Equation 2.5 describes the conversion for a long channel (Pe<1), with $\mu_1$ representing the asymptotic Sherwood number (Sh at fully-developed conditions) divided by 4, $\chi_m$ being the mixing cup exit conversion of primary reactant, $\alpha_1$ being the first normalized Fourier weight and Pe being the transverse Peclet number $P_e=ReSc$.

$$1 - \chi_m \approx \alpha_1 \exp \left( -\frac{\mu_1}{Pe} \right)$$

(2.5)

$\alpha_1$ becomes a tuning factor, which the authors found to be around 0.8. However, with the inclusion of the first normalized Fourier weight, the degree of computational complexity needed to obtain a solution that is close to the experimental data still limits the practical applicability of the 1-D model.

A 2004 study by Bhattacharya, Harold and Balakotaiah included effects of channel geometry along with the first normalized Fourier weight. These effects were neglected in several prior works, but can have a significant effect on the predictive capability of the model. The impact of non-uniform washcoat thickness was studied, and a shape-normalized, transverse diffusion length scale-dependent correlation was derived to eliminate the effects of
the two-dimensional washcoat geometry. Relevant assumptions included variable washcoat thickness across the cross-section of an arbitrary-shaped channel, uniform thickness along the channel length, isothermal reaction and constant-velocity along the channel length. The rate constant (k) was constant, as a result of isothermal reaction. Danckwert’s boundary condition was applied in the fluid phase, as was a no-flux condition at the ends of the washcoat. The authors confirmed the conclusions of West, Balakotaiah and Jovonovic (2003) that the first normalized Fourier weight should be on the order of 0.8 instead of the previously-used value of one. A significant outcome of this study was that the geometry of a non-uniformly coated monolith channel may be approximated by a circular, uniformly-coated channel for the fully-developed velocity profile and developing thermal profile (Bhattacharya et al., 2004a and Hayes and Kolaczkowski, 1994). This conclusion was significant in that the channel coating geometry, for the conditions of the authors’ study, did not impact the predicted results.

In addition to the outcomes described above, the Bhattacharya et al. study (2004b) provided insight into the shortcomings in the 1-D two-phase (solid/gas) approach method. The study describes two fundamental shortfalls in this solution method: the assumption that the first normalized Fourier weight should have been ~0.8 instead of 1, leading to errors of 20-30% in conversion predictions. The second error was caused by the use of an incorrect transport coefficient. Bhattacharya et al. stated that neither the constant temperature nor flux conditions are independently representative of the boundary conditions, but are asymptotic and are functions of both flow and washcoat geometries, respectively. This conclusion was
consistent with the outcomes of the Balakotaiah et al. (2000) and Gupta and Balakotaiah (2001) studies.

2.2 2-D Convection-Diffusion with Wall Reaction Approach

The second approach methodology to approximate the behavior of the wall reaction inside a tube is the 2-D convection-diffusion with wall reaction. The general steady state equations (in cylindrical coordinates) are given below, and include variable thermophysical properties.

Continuity:

$$\frac{1}{r} \frac{\partial}{\partial r} (\rho r u_r) + \frac{\partial}{\partial z} (\rho v_z) = 0$$  \hspace{1cm} (2.5)

Momentum conservation:

$$\left( \rho u_r \frac{\partial u_r}{\partial r} + \rho v_z \frac{\partial u_r}{\partial z} \right) = -\frac{\partial P}{\partial r} + \left[ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (\rho r u_r) \right) + \mu \frac{\partial^2 u_r}{\partial z^2} \right]$$  \hspace{1cm} (2.6)

$$\left( \rho u_z \frac{\partial v_z}{\partial r} + \rho v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial P}{\partial z} + \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( \rho \mu \frac{\partial v_z}{\partial r} \right) + \mu \frac{\partial^2 v_z}{\partial z^2} \right]$$  \hspace{1cm} (2.7)

Energy conservation:

$$\left( \rho c_p u_r \frac{\partial T}{\partial r} + \rho c_p v_z \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right)$$  \hspace{1cm} (2.8)

Species conservation:

$$\left( \rho u_r \frac{\partial \omega_A}{\partial r} + \rho v_z \frac{\partial \omega_A}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_A \frac{\partial \omega_A}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho D_A \frac{\partial \omega_A}{\partial z} \right)$$  \hspace{1cm} (2.9)
Correlations for the Nusselt (Nu) and Sherwood (Sh) numbers can again be derived following simplification and solution of the transport equations, relating the differences in temperature and concentration into heat and mass transfer coefficients and translated into the local Nu and Sh numbers.

Prandtl developed the boundary layer equations in the early 20th century, and his work yielded the first practical solution of viscous flow problems (Raja, Kee, Deutschmann, Warantz and Schmidt, 2000). The approximations, detailed in a 1968 text by Schlichting, have become commonplace in fluid transport theory. As flow dependence on viscosity is decreased (increasing Reynold’s number), the approximations become increasingly valid.

The assumptions for the 1-D two-phase solid/gas approach discussed in the previous section are still valid here, with the exception of the inclusion of radial diffusion in the 2-D case. Therefore, the primary difference in the two methods is that the 2-D method includes diffusion in the radial direction. The 1-D two-phase approach assumes that the diffusive transport is assumed to be so dominant that no radial variations in the species composition exist in either direction, and thus the effects are approximated by a lumped parameter in the rate equations.

Radial diffusion is captured in the 2-D equations as second-order derivatives in the radial direction. Elimination of the axial diffusion terms (the second-order terms in z in equations (2.6)-(2.9) converts the elliptic Navier-Stokes equations into the parabolic boundary layer equations, a simplification that greatly decreases the computational complexity of the equations’ solution. The study conducted by the Raja et al. (2000) and Balakotaiah, Gupta and West (2000), among others, supports this approach. Section 3.3.5 discusses the validity of this approach in detail. The fundamental 2-D approach, first
described in Damköhler’s work in 1937, was revisited by Heck et al. in 1976 and Lee and Aris in 1977 and was later extended to shape the current state of the art by, among others, Hayes et al. in 1992 and Balakotaiah et al. in 2000. The equations, presented in cylindrical coordinates, aim to approximate the temperature/concentration gradients by accounting for radial diffusion. The primary benefit gained from eliminating axial diffusion terms becomes enabling the problem to be solved with decreased computational difficulty, while maintaining account for physically relevant parameters, such as radial diffusion. Raja et al. (2000) states that the boundary layer assumptions are valid at Reynolds’s numbers on the order of 100 or more.

Heck et al. presented an extension of Damköhler’s ground-breaking use of the boundary layer equations for two-dimensional flow in a 1976 study focused on the oxidation of carbon monoxide and hydrocarbons for catalytic monolith reaction application. The authors developed a steady-state two-dimensional model to compare the predicted results with those of a 1-D model also presented. The authors stated that the 2-D model requires substantially increased computation time, and if in close agreement with the simpler 1-D model, it may not need to be used for the application described in the study.

The model was patterned after the classical Graetz problem of flow through a tube. The model included gradients in the axial and radial directions, and neglected axial conduction/diffusion, in accordance with the boundary layer assumptions. Flow was assumed to be incompressible, fully developed, and fall into the laminar flow regime. The transport parameters can be found from the radial and axial gradients. The model was solved using a two-dimensional finite difference technique. The expressions are dependent on the
Graetz number, and are derived from the well-known constant wall temperature and constant flux cases. The Arrhenius-type kinetic model used in the authors’ study was derived by Voltz for the carbon monoxide oxidation reaction.

A major constraint outlined by the Heck et al. study is that the correlations and solution behaviors were heavily dependent on the reaction rate. Since the Heck group’s work investigated an oxidation reaction, the results are slightly different than those expected for the SMR case. The authors also outlined the significant conclusion that axial conduction in the gas phase should have little bearing on the model prediction, validating use of the boundary layer assumptions.

Following the Heck et al. study of 1976, Lee and Aris published a theoretical study in 1977 based on a straight-tube model of the highly exothermic CO oxidation reaction. Significant assumptions of this approach, like the Heck et al. study, included incompressible, fully developed laminar flow, negligible axial conduction/diffusion in the fluid. The boundary conditions included both symmetry and a reaction rate-dependent wall temperature condition. Again, the dependence of the equations on the reaction rate outlined the importance of using an appropriate and accurate kinetic model. The kinetics were approximated using a single, first-order irreversible reaction assumption. For models including precious-metal catalyst, the reaction rate equation was modified.

The equations were solved using a computationally-intensive iterative solution based on the principles of the Kummer’s confluent hypergeometric functions. The Newton-Rhapson iteration method was employed to reduce the number of elements in the two-dimensional models. Lee and Aris’ study raises visibility of the transport coefficients
approaching their asymptotic values at the constant flux and temperature/concentration boundary conditions. The kinetics were described with a singular adsorption parameter in the Arrhenius expression. The authors also stated that the reaction rate model provided the deviation from the asymptotic Nusselt and Sherwood numbers. The significance of this point was studied in later works (summarized below), and underscored the significance of an appropriate kinetic model for accurate modeling.

Hayes, Kolaczkowski and Thomas (1992) continued the study of 2-D transport with wall reaction in the channel of a catalytic monolith. The authors used a finite element model to describe the geometry, and studied various solution schemes for comparison. Relevant assumptions include thermally fully-developed flow, radial gradients due to fast catalytic wall reaction, adiabatic channel wall, homogeneous reaction and negligible axial diffusion. The Galerkin finite element method was used to solve the advection-diffusion transport equations. The ideal gas equation of state was also implemented for the propane combustion reaction. A one step reaction model was used for both the heterogeneous and homogeneous reactions. Due to the wall gradients, the authors cited implementing a variable element size as a better approximation of the transport and reaction at the wall (example shown in Fig. 2.3).
Hayes et al. also introduced taking known transport coefficient results for conventional (respective) constant wall temperature and flux boundary conditions of 3.66 and 4.36 as a method of model feasibility validation. This method was proven to validate the model within 1% of the nominal transport coefficient values. Significant outcomes of the 1992 Hayes et al. study include the notion that the wall reactant concentration is non-zero and that the fully-developed transport coefficients are not coincident with either the constant flux or the constant wall temperature/concentration case; future studies found that those cases bound the actual solution. The latter outcome, in combination with the Lee and Aris study, has led to later studies of the relation of the transport coefficients to the Dirichlet and Neumann boundary conditions.
In 1998, Karabulut and Ataer extended the prior works to utilize a two-dimensional finite difference method to numerically solve the boundary layer equations, with the aim of deriving the temperature and velocity profiles and the local transport coefficients. Relevant assumptions in their work included ideal gas, constant wall temperature boundary condition, fully-developed hydrodynamic flow and azimuthal symmetry. Axial conduction was neglected, in accordance with the boundary layer assumptions. The differencing scheme was taken by expanding a Taylor series around the velocity components at the center of an element and linking them to the adjacent nodes. The large matrices were solved (by inversion) once to give the discretized solutions for velocity and temperature parameters.

This solution methodology is advantageous due to the ease of solving the second-order boundary conditions and potential for improving the stability by varying the radial element spacing to increase the element density near the channel wall. Using a non-uniform grid allows implementation of a decreased number of elements, which dramatically reduces the degree of computational complexity. An important conclusion of the Karabulut and Ataer study was that the thickness of thermal boundary layer is greater than the hydrodynamic boundary layer, justifying the fully-developed velocity profile. The authors then used the ratio of thermal boundary layer thickness to tube radius to validate the use of cylindrical coordinates, and they stated that the use of cylindrical coordinates for laminar flow conditions in pipes with low diameter-to-length ratios is appropriate, as the precision of the results is sufficient.

Although validation of the fully-developed hydrodynamic boundary layer was a critical contribution of the Karabulut and Ataer study with regard to this thesis, its primary
outcome was the implementation of matrix solution scheme for the two-dimensional transport equations.

In 1999, Hayes and Kolaczkowski presented a 2-D model with an axisymmetric condition with a first-order wall reaction of methane combustion in air. Additionally, a simplified one-step Arrhenius-type mechanism was used for the reaction rate. Important assumptions in the Hayes and Kolaczkowski study were: steady state flow in a circular tube, no homogeneous reaction, axisymmetry, adiabatic channel, no radiation, no diffusion in the washcoat and ideal gas. Implementing the boundary layer assumptions eliminate the axial conduction terms.

The Galerkin finite element method was used to solve the reactor model. The results of the Hayes and Kolaczkowski study outlined an important characteristic of the local Nusselt number. The authors found that the Nusselt (and Sherwood) number changes depending on whether the thermal boundary layer develops alone or in conjunction with the hydrodynamic boundary layer. The authors’ study assumed a developing thermal boundary layer with hydrodynamically fully-developed flow. This simplification of the actual monolith flow behavior will be used for the current study. For each case, the unique solution could be found by plotting the transport coefficient against the inverse Graetz number. The results for Nusselt and Sherwood number were presented in that format.

The plot of Nusselt and Sherwood vs. inverse Graetz number (inverse of the hydraulic diameter to length ratio times the product of Reynolds and Prandtl/Schmidt), shown below, confirmed that the transport coefficients are of the same magnitude as the constant wall temperature (Nu=3.66) and constant wall flux (Nu=4.36), but did not match either case as
neither of the two wall boundary conditions represents the actual condition. A follow-on study, which used an interpolation between the constant wall temperature and constant wall flux boundary conditions, used the Damköhler number at the inlet reactor conditions to approximate the transport coefficients. This method did not match the experimental data to which the model was compared. Another important outcome of the 1999 Hayes and Kolaczkowski study was the confirmation of minimal variation in Nusselt number along the channel at laminar, fully-developed flows in reacting systems. The coefficients varied by about 18% from the average. Further, the plot of Nusselt vs. inverse Graetz showed significant variation in the curves, whereas coincident behavior was expected if the inlet temperatures are constant. Figures 2.4-5 illustrate this trend.

Figure 2.4: Inlet concentration effect on transport coefficient, at 700K gas inlet temperature and 1 m/s velocity. Run 1 CH₄ mole fraction: 0.001, Run 2: 0.005, Run 3: 0.01 (Hayes and Kolaczkowski, 1999)
The idea that the constant wall temperature/concentration and constant heat flux boundary conditions are of the same order as the experimental data has led to further work in that area. A 2000 study by Balakotaiah, Gupta and West compared a 2-D convection-diffusion for short monoliths (high GHSV) to a general 2-D model and a 1-D two-phase solid/gas model. A 2-D model was formulated with the following assumptions: first-order reaction, constant properties, azimuthal symmetry, adiabatic channel and steady state. A flat velocity profile was also assumed in the study.

The authors’ general model was found to be bounded by the short monolith case and the 2-D convection model, a discovery that supports Hayes’ and Kolaczkowski’s works (1992, 1999). Including diffusion was the major simplification between the 1-D two-phase model and the two-dimensional models. The primary outcome of their study was that in the mass transfer-controlled regime, conversion was only dependent on the transverse Peclet number, which is the inverse of the Damköhler (Da) number in the radial direction. The
parameter is cited by the authors as the most important parameter in the design of catalytic monoliths. This premise provides the fundamental motivation for this study; that an accurate representation of the radial diffusion can dramatically improve the predictive capability of reactor models and should be included when designing and sizing reactors.

Balakotaiah continued his work with Gupta in 2001 with their theoretical study which was aimed at deriving transport coefficients in catalytic monoliths. A primary objective of their study was to confirm the asymptotic behavior of the transport coefficients for a catalytic monolith reactor. The authors raised the point that assuming a constant value for the transport coefficient at the reactor inlet may lead to erroneous results for combustion reactions. The asymptotic solution was found not to be coincident with either the constant temperature boundary condition or the constant flux condition, reaffirming the conclusions of Hayes and Kolaczkowski (1999) and Balakotaiah et al. (2000). The boundary conditions and model assumptions were coincident with those of the 2000 Balakotaiah et al. study, and the primary outcomes of the study helped to define the approach methodology of the research in this thesis. The Gupta and Balakotaiah work was an extension of the 2000 Balakotaiah study, with increased focus on the behavior of the transport coefficients along the axial cylinder position. The authors’ work also expands upon the principle that the transport coefficients are constant at low Reynold’s numbers. The authors concluded that the constant value was a fair approximation of the transport behavior, but the coefficients were actually taken at the asymptotic values for cases where the cylinder length exceeded its diameter by two orders of magnitude. This study neglected velocity, axial position and reaction
parameters, and the authors cited these as fundamental sources of error in the predicted results.

The reaction rate term, taken from the Balakotaiah et al. study (2000), was an Arrhenius type one-step, first-order combustion reaction mechanism. Figure 2.6 illustrates the dependence of the Sherwood number (including reaction kinetics influence) on the dimensionless axial coordinate for a parabolic velocity profile (fully-developed flow).

![Figure 2.6: Dependence of the Sherwood number on dimensionless axial coordinate for the convection model (no axial diffusion) with parabolic velocity profile (Gupta and Balakotaiah, 2001). Φ is the Thiele Modulus, and is analogous to the Damköhler number.]

The authors also stated that the Sherwood number may vary substantially for developing flow in the entrance region.

The final significant result concluded in the Gupta and Balakotaiah study was the discovery of azimuthal symmetry, an assumption included in the current work. Many of the studies analyzed in this literature review utilized this boundary condition, but the 2001 Gupta
and Balakotaiah work found that this assumption may be susceptible to instabilities caused by azimuthal perturbations; this would necessitate using the full three-dimensional Navier-Stokes model. This behavior is magnified by the presence of homogeneous reactions or a multiple-reaction mechanism. The azimuthal symmetry condition limits the applicability of the boundary layer approach to geometries like the long, round tube. Neglecting homogeneous reactions has been validated numerous times in the literature for their respective reaction mechanisms and should mitigate the concern for the symmetry condition.

Emphasis on the coupling features of the transport with reaction was presented in a 2002 analysis by Tomašić, Gomzi and Zrnčević. To study the coupling behavior, a two-dimensional, heterogeneous model was developed for nitric oxide decomposition with the following assumptions: steady-state, isothermal reaction, simultaneous mass transfer and chemical reaction at the catalyst sites, fluid-phase radial diffusion and the key boundary layer assumption of negligible axial diffusion. A one-step Langmuir-Hinshelwood reaction model was used to describe the reaction rate, and the Chapman-Enskog formula to determine the molecular diffusion coefficient. The effective coefficient was found from the parallel pore formulation. Their model was compared to experimental results performed for that study. The assumptions and reaction model gave rise to some significant conclusions. First, the concentration gradients were higher in the fluid phase than in the washcoat, suggesting that the reaction rate was primarily limited by interphase diffusion. Next, the influence of homogeneous diffusion was not significant, reaffirming the conclusions of earlier studies. Last, the authors concluded that the two-dimensional model sufficiently approximated the convection-diffusion reactor conditions for the studied nitric oxide reduction reaction.
The authors also stated that the 2-D model is capable of identifying the effects of individual processes, such as the individual impact of the reaction or the interphase transport. This facet is beneficial to the current work, as the sensitivities to both transport and reaction are needed for accurate correlation derivation. The authors concluded that the 2-D model is sufficient to predict the behavior of heterogeneous transport and chemical reaction.

Previous works have shown that though the entrance effects were significant for thermally developing flow transitioning to fully-developed flow within the control volume, the reaction characteristics were dominant within the fully-developed region. Prior models implemented correlations for each characteristic over the entire reactor length, mainly by using a form of a Damköhler interpolation described in the 1999 Hayes and Kolaczkowski study. Most historical studies were successful for a limited range of reaction conditions, but the focus in the literature remains on deriving a universal correlation that captures the reaction characteristics and the transport behavior. This emphasis led to a 2006 study by Benedetto, Marra, Donsì and Russo. A fast exothermic surface reaction was modeled in two dimensions utilizing a two-zone modeling approach. Propane combustion was taken as the model reaction, which may limit the applicability of the specific results to the current work. Two zones were used to represent the conditions of the heat transfer efficiency. The first (pre-ignition) zone approximated the constant heat flux boundary condition, while the second (post-ignition) zone was similar to constant wall temperature. The model assumptions included steady state (though initially the unsteady equations are presented), negligible homogeneous reaction, ideal gas, and a first-order one-step reaction model was used to represent the reaction kinetics.
The contributions of the Benedetto study include describing the effect of radial gradients in the entrance region and confirming the applicability of a Damköhler interpolation in the fully-developed region. Because this approach was focused on a combustion reaction, its appropriateness in the context of current work is not readily known. However, a continuation of the current study may involve the use of two zones to describe the transport-controlled and the kinetically-controlled regimes to increase the predictive accuracy of the model, perhaps with the first zone in the entrance region and the second in the developed region.

The studies reviewed in this chapter typically investigated transport coefficient development of systems utilizing combustion reaction schemes. Still, neglecting homogenous reaction, using the ideal gas equation of state, steady-state flow and azimuthal symmetry were repeatedly implemented and validated for the authors’ specific cases. The current study will employ all of these assumptions. This work will extend the prior work to include an improved wall boundary condition, a non-isothermal, low-pressure SMR reaction, reactor geometry with complex boundary conditions used to derive local transport coefficients that include reaction effects, and employ a new solution methodology for this type of problem that includes radial diffusive effects without relying on computationally-intensive solving schemes such as the one conducted by the Raja group discussed in Section 3.3.5.
3. MODEL FORMULATION AND SOLUTION METHODOLOGY

3.1 Transport Equations and Transport Coefficient Definition

The respective definitions of the mass and heat transfer coefficients and dimensionless concentration and temperature gradients Sherwood and Nusselt number, presented in Chapter 1, are:

\[
h = \frac{k_{\text{wall}}}{T_{\text{wall}} - T_{m}} \left. \frac{\partial T}{\partial r} \right|_{r=R} \quad \text{and} \quad h_{\text{mass, A}} = \frac{D_{A, \text{wall}}}{\rho_{A, \text{wall}} - \rho_{A, \text{m}}} \left. \frac{\partial \rho}{\partial r} \right|_{r=R}
\]  \quad (1.9)

\[
Sh_{\Lambda} = \frac{h_{\text{mass, A}} d_{h}}{D_{A, \text{film}}} = Sh_{\Lambda}(z, Re, Sc)
\]

\[
Nu = \frac{h d_{h}}{k_{\text{film}}} = Nu(z, Re, Pr)
\]  \quad (1.10)

\(D_{A}\) and \(k\) in equation (1.9) are evaluated at the wall conditions.

3.1.1 Boundary Layer Equations and Fundamental Assumptions

The mathematical representation and simplification of the coupled convection-diffusion problem determines the accuracy and validity of the calculated transport coefficients. Specifically, an appropriate approximation of the studied geometry is the critical step toward beginning the transport formulation. For the case of the catalytic monolith channel, an infinitely long round tube geometry is commonly used in historical
approximations of a catalytic monolith channel (Hayes and Kolaczkowski, 1994, Bhattacharya, Harold and Balakotaiah, 2004b), which resembles the annular fin. The model geometry will be described in detail in the following section. While at first glance the geometry is quite complex, the washcoat rounds the corners of the channel walls, so that the gas flow cross-section coarsely approximates a round channel (Hayes and Kolaczkowski, 1994).

So, the model equations begin with the 2-D cylindrical Navier-Stokes equations for constant-density and constant-dynamic viscosity flow without viscous dissipation (constant through each cell, updated along axis), presented below (Bird, Stewart and Lightfoot, 2007).

Continuity:

\[
\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r) + \frac{\partial}{\partial z} (\rho v_z) = 0 \tag{3.1}
\]

Momentum conservation:

\[
\frac{\partial}{\partial t} (r \rho v_r) + \frac{\partial}{\partial r} (r v_r) + \frac{\partial}{\partial z} (v_z v_r) = - \frac{\partial P}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} \left( \rho \mu \frac{\partial v_r}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho \mu \frac{\partial v_r}{\partial z} \right) + \rho g_r \tag{3.2}
\]

\[
\frac{\partial}{\partial t} (r \rho v_z) + \frac{\partial}{\partial r} (r v_z) + \frac{\partial}{\partial z} (v_z v_z) = - \frac{\partial P}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( \rho \mu \frac{\partial v_z}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho \mu \frac{\partial v_z}{\partial z} \right) + \rho g_z \tag{3.3}
\]
Energy conservation:

\[
\frac{\partial}{\partial t} \left( \rho c_p T \right) + \frac{\partial}{\partial r} \left( \rho c_p v_r T \right) + \frac{\partial}{\partial z} \left( \rho c_p v_z T \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( r k \frac{\partial T}{\partial z} \right)
\]  

(3.4)

Species conservation:

\[
\frac{\partial}{\partial t} \left( \rho \omega_\lambda \right) + \frac{\partial}{\partial r} \left( \rho v_r \omega_\lambda \right) + \frac{\partial}{\partial z} \left( \rho v_z \omega_\lambda \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_\omega \frac{\partial \omega_\lambda}{\partial r} \right) + \frac{\partial}{\partial z} \left( r \rho D_\omega \frac{\partial \omega_\lambda}{\partial z} \right)
\]  

(3.5)

The conservation equations are simplified according to the following assumptions:

- Smooth, right cylinder geometry
- Boundary layer assumptions
- Two-dimensional
- Steady state
- Ideal gas
- Azimuthal symmetry
- External heat source included in wall boundary condition
- Negligible homogeneous reaction (including catalyst)
- Negligible radiation
- Negligible gravity dependence

The boundary layer assumptions provide the basis for the computational simplicity in the current approach. Boundary layer equations are a sufficient intermediate between the 1-D approach, which does not accurately account for transport to the wall, and the 2-D Navier-Stokes equations (Raja, Kee, Deutschmann, Warantz and Schmidt, 2000). The fundamental
basis for the boundary layer approach is that axial diffusion is neglected, while account for radial transport is made. Neglecting axial diffusion changes the transport equations from elliptic to parabolic, simplifying the solution to the equations without appreciably compromising accuracy, as seen in the Raja et al. study (2000). Neglecting radial diffusion causes the plug-flow model to over-predict reactor performance, as the diffusive transport determines the rate of the reacting species being carried to the channel wall (Raja et al., 2000). Also, the geometry considered in this study contains a thin, 0.15mm thick catalyst layer, which represents 1.5% of the tube diameter modeled in this thesis. Due to the washcoat being so thin, it is reasonable to neglect homogeneous diffusion through the washcoat (Tonkovich, 2007). The boundary layer approximations for the 2-D long tube in cylindrical coordinates are listed below (Incropera and Dewitt, 2002).

\[ \nu_z \gg \nu_t, \]
\[ \frac{\partial \nu_z}{\partial r} \gg \frac{\partial \nu_z}{\partial z}, \frac{\partial \nu_r}{\partial r}, \frac{\partial \nu_r}{\partial z}, \] \[ \frac{\partial T}{\partial r} \gg \frac{\partial T}{\partial z}, \] \[ \frac{\partial \rho_A}{\partial r} \gg \frac{\partial \rho_A}{\partial z}. \]

Velocity boundary layer \hspace{1cm} \text{Thermal boundary layer} \hspace{1cm} \text{Concentration boundary layer}

The Raja study compares the boundary layer equations with the full Navier-Stokes solution, with close approximation. Further justification for this approach is given in Section 3.3.3.

Simplification of the Navier-Stokes equations by the assumptions given above yields the design equations for this study, which are shown below.
Continuity: [trivial solution] (3.6)

Momentum:
\[
0 = -\frac{\partial P}{\partial z} + \mu \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z}{\partial r} \right) \right] \quad \text{axial} \quad (3.7)
\]
\[
0 = -\frac{\partial P}{\partial r} \quad \text{radial} \quad (3.8)
\]

Energy:
\[
\frac{\partial}{\partial r} \left( \rho c_p u_z T \right) + \frac{\partial}{\partial z} \left( \rho c_p u_z T \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( rk \frac{\partial T}{\partial r} \right) \quad (3.9)
\]

Species:
\[
\left( \rho u_r \frac{\partial \omega_A}{\partial r} + \rho u_z \frac{\partial \omega_A}{\partial z} \right) = \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r\rho D_A \frac{\partial \omega_A}{\partial r} \right) \right] \quad (3.10)
\]

Further simplification to the momentum equations can be made by assuming fully-developed hydrodynamic flow at the channel inlet, while maintaining developing thermal and mass flow (Hayes and Kolaczkowski, 1999). Because fluid is assumed to enter the tube at a uniform temperature and the surface temperature is set by a locally-constant temperature wall profile (described below) coupled with heat generated from the chemical reaction, a thermal boundary layer is expected to develop. The fully-developed velocity profile yields an initially parabolic shape, which dramatically improves the computational efficiency of the model. The validity of this simplification could be the subject of future work. The \( u_r \) and \( \frac{\partial u_z}{\partial z} \)-terms in both the energy and species concentration equations are also negligible as a result of the boundary layer assumptions. The continuity and momentum conservation
equations given above can then be reduced to a single equation, 3.11, which (when
rearranged) expresses the fully-developed hydrodynamic flow in terms of \( \nu_z \) as a function of
radial position, \( r \) (Incropera and Dewitt, 2002):

\[
\nu_z(z, r) = 2\nu_{zm}(z) \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \quad (3.11a)
\]

where \( \nu_{zm}(z) = \frac{m}{\rho_m(z)A_{\text{flow}}} \quad (3.11b) \)

Mean velocity in equation 3.11a and density in equation 3.11b vary with position due to
temperature change from the ideal gas state equation to preserve mass conservation.

3.1.2 Boundary and Initial Conditions

In accordance with the assumptions listed above, the boundary and initial conditions are
shown below.

**Inlet Condition:**
\[
\rho_A(0, r) = \rho_{A_0} \\
T(0, r) = T_0
\]

**Quenched Reaction:**
\[
\frac{\partial \rho_A}{\partial z}(L, r) = 0 \\
\frac{\partial T}{\partial z}(L, r) = 0
\]

(3.12)

(3.13)
Axial Symmetry:  
\[ \frac{\partial \rho_A}{\partial r} (z,0) = 0 \]  \[ \frac{\partial T}{\partial r} (z,0) = 0 \]  

Wall Condition:  
\[ \rho_A (z, R) = \rho_{A\text{wall}} (z) = \rho_A (z, R - \Delta r) + \left[ \sum_{n=1}^{3} \left( \frac{v_A n r_n}{D_A} \right) \right] \frac{q_{\text{exh}}}{A_{\text{surf}}} \Delta r_{\text{bed}} \]  
\[ T(z, R) = T_{\text{wall}} (z) = T(z, R - \Delta r) + \left( \frac{q_{\text{exh}}}{k_{\text{exh}}} + \sum_{n=1}^{3} \frac{q_{\text{rxn,n}}}{k_{\text{rxn,n}}} \right) \frac{1}{A_{\text{surf}}} \Delta r \]  

The wall temperature profile given by equation 3.15 is derived from the assumption that the wall temperature profile along the axial reactor direction is equal to the FEA model gas temperature profile described by Valensa (2009) which accounts for the externally supplied thermal energy, as well as the enthalpies of reaction. It should also be noted that the energy generation term due to chemical reaction is only considered at the channel wall. The energy generation term that combines the known formation enthalpies and the reaction rates, represented by \( r_n \), for each reaction in the three-step kinetic mechanism described in Section 3.2. Furthermore, a species conservation equation exists for each reacting component in the kinetic mechanism, whose reaction rates are represented by \( r_A \). The species reaction rates are given by a composite of the overall reaction rates that contains the specific species. For example, since CO is a product in the SMR reaction and a reactant in the WGS reaction, the rate of formation of CO is given by: \( r_{\text{CO}} = r_1 - r_2 \). Reactants are designated as the negative rate;
products have a positive rate. $\eta$ is an experimentally-derived correlation correction factor to match the nickel-catalyst mechanism to the precious metal-containing data (Valensa, 2009).

### 3.1.3 Bulk Fluid Parameters

$T_m$ and $(\rho_{m,A})$ are approximated by mass-averaging the radial temperature (and density) sums at each axial location over the total mass, as represented by equation 3.16 (Indropera and Dewitt, 2002). $T_{i,j}$ is the local temperature, $nr$ is the total number of radial steps, $i$ is the axial position and $j$ is the radial position. Because the radial cell size is constant, simply summing the radial temperatures at a given axial location and dividing by the total number of radial steps is appropriate.

$$T_{m,i} = \frac{1}{\nu_{z,m} \rho_{m} c_{P,m} A_{flow}} \int_{A_{i}} \rho c_p \nu_{z} T \text{d}r = \frac{2}{\nu_{z,m} R^2} \sum_{j=1}^{nr} \left( \rho_{i,j} c_{P[i,j]} \nu_{z[i,j]} T_{i,j} \left( j^* \text{d}r \right) \right) \tag{3.16}$$

Mean temperature and species density are required to calculate the local convective heat and mass transfer coefficient from equation 1.9.
3.1.4 Thermophysical Properties

The thermophysical properties thermal conductivity, viscosity, enthalpy and specific heat used in the current work are taken from temperature-dependent correlations in Daubert and Danner (1989). Mixing rules for thermal conductivity and dynamic viscosity were taken from Poling, Prausnitz and O’Connell (2001), and are listed below in equations 3.17-3.18. A simple mass-averaging of the composite heat capacities is acceptable (Poling et al., 2001). MW is molecular weight.

**Dynamic viscosity:**

\[
\mu_{\text{mix}} = \sum_{i=1}^{5} \frac{y_i \mu_i}{\sum_{j=1}^{5} \left( y_j \varphi_{ij} \right)}
\]  \hspace{1cm} (3.17a)

\[
\varphi_{ij} = \frac{\left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{0.5} \left( \frac{\text{MW}_j}{\text{MW}_i} \right)^{0.25} \right]^2}{\left[ 8 \left( 1 + \frac{\text{MW}_i}{\text{MW}_j} \right)^{0.5} \right]}
\]  \hspace{1cm} (3.17b)

**Thermal conductivity:**

\[
k_{\text{mix}} = \sum_{i=1}^{5} \frac{y_i k_i}{\sum_{j=1}^{5} \left( y_j A_{ij} \right)}
\]  \hspace{1cm} (3.18a)
Binary diffusivities are found from the Lennard-Jones parameters, taken from Bird, Stewart and Lightfoot (2002). The parameters are listed in Appendix A. The binary coefficients for each of the 10 combinations were determined by the equation in the Appendix A, and curve fit to a second-degree polynomial for a temperature range of 600-1200K. The individual species diffusivities for the mixture are calculated per equation 3.19, also taken from Poling, et al. (2001), and use the 10 binary diffusivities found by the curve fits referenced above.

**Diffusivity:**

\[
D_{i,\text{mix}} = \left( \sum_{j=1 \neq i}^{4} \frac{y_j}{D_{ij}} \right)^{-1}
\]  

(3.19)

### 3.2 Catalytic Surface Reactions and the LHHW Kinetic Mechanism

In a general sense, catalytic surface reactions undergo the following steps (Fogler, 1999):
1. Mass transfer of reactant species from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore surface through the catalyst pores to the immediate vicinity of the internal catalyst surface
3. Adsorption of reactant onto catalyst surface
4. Reaction on catalyst surface
5. Desorption of the products from the catalyst surface
6. Diffusion of the interior products form the interior of the pellet to the pore opening at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

These steps are typically simplified for computational efficiency. The Langmuir isotherm, published in 1916, is used to model gases adsorbed on solids. The major assumptions included in his model are (Froment and Bischoff, 1990 and Pilling and Seakins, 1995):

A. The surface of the adsorbent is uniform (all the adsorption sites are equivalent)
B. Adsorbed molecules do not interact
C. All adsorption occurs through the same mechanism
D. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent
Though these four conditions are seldom simultaneously true, comparing the predictive results of the Langmuir mechanism with the Eley-Rideal model (and others) has led to the former emerging as the preeminent choice for modeling surface adsorption. As a result, the kinetic mechanism chosen for the current study is a Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism developed by Xu and Froment (1989a-b). Coupling of the heterogeneous reaction kinetics with the convection-diffusion behavior occurs through the reaction rate terms at the end of the energy and mass boundary condition equations (3.15). The LHHW form was constructed by Hinshelwood, who proposed a mechanism based on Langmuir’s adsorption principles, and this model was made popular by Hougen and Watson. To date, this is the predominant mechanism used in the fuel cell industry for steam methane reforming reactions. The Xu and Froment mechanism was developed for nickel catalyst, and the current work correlates differences between nickel and precious metal catalyst with the $\eta$ term. The thin washcoat layer seen on the Modine coated reactor is on the order of 10-30 $\mu$m, a thickness that justifies neglecting diffusion through the catalyst layer (Hayes and Kolaczkowski, 1999). The Langmuir assumptions (A-D) condense the above catalytic surface reaction steps (1-7) into the following five stages:

1. Mass transfer of reactant species from the bulk fluid to the external surface of the catalyst pellet
2. Adsorption of reactant onto catalyst surface
3. Reaction on catalyst surface
4. Desorption of the products from the catalyst surface
5. Mass transfer of the products from the external pellet surface to the bulk fluid

These assumptions gave rise to the Xu and Froment mechanism, which provides reaction rates for three relevant equilibrium reactions. The primary reaction is the endothermic SMR reaction (R\textsubscript{1}), which takes place between 700-900°C (since an external heat source provides the necessary heat to achieve the desired conversion, the wall temperature is greater than the mean fluid temperature). As a result, at higher temperatures, the reaction provides an equilibrium conversion that favors hydrogen production. Additionally, the reaction is pressure-dependent in accordance with LeChatelier’s Principle (Fogler, 1999). This principle states that since there are four moles of products against only two moles of reactants, the reaction tends toward the products at low pressures. The high-temperature, low-pressure conditions also validate the use of the ideal gas equation of state.

The second reaction in the Xu and Froment LHHW mechanism is the exothermic water-gas shift (WGS) reaction (R\textsubscript{2}), which occurs between 300-375°C. Due to its low temperature range, however, the WGS reaction limits the temperature range of operation for systems which follow the behavior of this mechanism. Although the higher temperatures shift the equilibrium favorably for hydrogen production in the SMR reaction, these elevated temperatures decrease the effectiveness of the WGS reaction. A decreased shift toward WGS products would increase the undesirable CO/CO\textsubscript{2} ratio. The final point about the water-gas shift reaction is that because there are two products and two reactants, the reaction is pressure neutral. This reaction can be used in lower-temperature, higher pressure hydrogen
production applications in combination with a system that implements internal reforming, to eliminate the need for a separate SMR reactor.

The third reaction, the reverse methanation (complete SMR) reaction, (R4), was included by Xu and Froment to match the data used for mechanism formulation. An important note is that the mechanism was developed for a nickel catalyst, so the rates may need to be scaled to account for the precious metal (typically palladium and platinum for lower and higher temperatures, respectively) and/or washcoat diffusion effects. The catalyst effectiveness factor is determined by correlating the kinetic model results with the data presented in Figure 4.8. The reaction mechanism and rate expressions used for the current work are presented below:

Reaction 1: \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \) (R1)

Reaction 2: \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) (R2)

Reaction 3: \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \) (R4)
The kinetic properties are taken from the Xu and Froment papers (1989a-b). $K_{eq}$ terms are the equilibrium coefficients, $K_{CH_4}$, etc. are adsorption coefficients and $k_{SMR}$, etc. are the kinetic rate constants. All units are in SI except $R_u$, which is in J/kmol, and temperature for correlations should be in K. The kinetic parameters are listed below in Table 3.1.
The above mechanism is utilized in this study for both its computational simplicity and historical accuracy in describing the SMR reaction; it is the solution to the two-dimensional transport equations that is of interest, not the kinetic mechanism. Thus, for the detailed validation cases, this mechanism will also be used. Future work may include a more detailed mechanism, such as the one derived by the Deutschmann group (Hecht et al., 2005).

The chemical reaction is responsible for an energy generation (or consumption) term, as the SMR reaction is endothermic and the WGS reaction is exothermic, with the net
reaction being endothermic. This component, \( q_{\text{rxn}} \), represents the composite influence of the reactions, and is included in the wall boundary condition equation 3.15.

### 3.3 Solution Methodology

#### 3.3.1 Code Development

Following the simplification of the transport equations from the boundary layer and other pertinent assumptions, the design equations and boundary conditions derived above are given in partial differential equation form for the assumed straight-tube geometry. To solve the equations by the proposed method, the equations must be transformed into ordinary differential equations and discretized in both the radial and axial directions. This method will be discussed in more detail in the next section. After transforming the PDEs into ODEs, there are several assumptions inherent in the discretization scheme. The transport and kinetic equations are each solved in a single matrix inversion (of kinetic equation solution). This method has been used in numerical transport texts (Tannehill, Anderson and Pletcher, 1997, Patankar, 1980), and comparison of the results with experimental data or higher-order modeling has demonstrated the necessity to have an accurate meshing scheme (Bazhlekov et al., 1996). For the current method, the cell size in both directions remains constant throughout the channel. A proposed sensitivity study could employ a logarithmic or similarly-varying mesh in the radial direction to improve accuracy at the channel wall, with increased mesh density near the wall. The axial mesh size would remain constant over the
tube length, a valid assumption given the model’s negligence of axial diffusion. An example of the proposed sensitivity case to the mesh scheme was presented in Figure 2.3.

The ordinary differential equations are then input into a matrix and solved in MATLAB. This program was selected due to its proficiency in solving matrices. Solving the equations in this manner yields an array of position-dependent parameters at each step, which yield local values for the mass and heat transfer coefficients, which are defined in equation 1.9. The local coefficients can be used to directly determine the local transport correlations.

### 3.3.2 Full Matrix Finite Difference Method

The integration scheme used in the current work, described above, is taken from Stanoyevitch (2005). It is a fully-implicit central differencing approach, and it provides results that are more physically sensible than the well-known Crank-Nicolson for a broad range of time steps as all four boundaries are defined (Stanoyevitch, 2005). The four boundaries in the current work are represented by two Dirichlet and two Neumann conditions, eliminating the need for implementing a marching scheme like Crank-Nicolson where stability is a large concern. The wall concentration condition for the species equations is given by the kinetic mechanism translated into a concentration profile at the wall, while the wall temperature profile for the species equation is taken from Valensa (2009). The matrices are set up to simultaneously solve all the equations to reach an exact solution. The axial components of the partial differential equations given in equations 3.9-10 are transformed below into ordinary differentials (includes the simplifications for fully-developed
hydrodynamic flow from Eq. 3.11). Parameter $i$ represents the axial direction and $j$ represents the radial direction. The radial position, “$r$”, is defined as $r = (j-1)\Delta r$.

Energy:          (3.23)

\[
\begin{align*}
[T_{[i+1,j]} \left( \frac{\rho_{[i+1,j]} c_{[i+1,j]} u_{z[i+1,j]}}{2\Delta z} \right)] + [T_{[i-1,j]} \left( \frac{-\rho_{[i-1,j]} c_{[i-1,j]} u_{z[i-1,j]}}{2\Delta z} \right)] = \\
\frac{1}{r_{[i,j]}} \left[ \frac{r_{[i+1/2,j]} k_{[i+1/2,j]} (T_{[i,j+1]} - T_{[i,j]})}{\Delta r} \right] - \frac{1}{r_{[i-1/2,j]}} k_{[i-1/2,j]} \left( \frac{T_{[i,j]} - T_{[i,j-1]}}{\Delta r} \right)
\end{align*}
\]

Species:          (3.24)

\[
\begin{align*}
[\omega_{[i+1,j]} \left( \frac{\rho_{[i+1,j]} u_{z[i+1,j]}}{2\Delta z} \right)] + [\omega_{[i-1,j]} \left( \frac{-\rho_{[i-1,j]} u_{z[i-1,j]}}{2\Delta z} \right)] = \\
\frac{1}{r_{[i,j]}} \left[ \frac{r_{[i+1/2,j]} D_{[i+1/2,j]} (\omega_{[i,j+1]} - \omega_{i,j})}{\Delta r} \right] - \frac{1}{r_{[i-1/2,j]}} D_{[i-1/2,j]} \left( \frac{\omega_{[i,j]} - \omega_{[i,j-1]}}{\Delta r} \right)
\end{align*}
\]

where

\[
v_z = 2v_{z,m[i]} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
\]

(3.25)

Using the energy equation 3.23 as an example, the equation can be re-written by substituting the terms in brackets with a single letter, since the terms are assumed constant throughout each cell. The temperature (or concentration)-dependent terms are then moved to the left side of the equation, and the constants are moved to the right. The general form becomes:
\[ fT_{[i,j]} + aT_{[i,j-1]} + bT_{[i,j+1]} + cT_{[i-1,j]} + dT_{[i+1,j]} = e \] (3.26)

Dividing through by the coefficient of the central term, \( T_{[i,j]} \) yields the following, where a capital letter represents the lower-case letter in equation 3.26 divided by \( f \):

\[ T_{[i,j]} + AT_{[i,j-1]} + BT_{[i,j+1]} + CT_{[i-1,j]} + DT_{[i+1,j]} = E \] (3.27)

For the current problem, \( E=0 \). Considering a 5x5 matrix, the temperatures can be identified by defining a counting parameter, \( n \), to describe a temperature at a given location. For the current work, \( n=(i-1)*nr + j \) including boundaries. Each temperature location \( T_{[i,j]} \) is solved based on the remaining constituents in equation 3.27. Defining this parameter enables the extension of the code to accept different grid sizes. The middle of the matrix can then be fully-defined, with only the boundaries remaining. The grid of a 25x25 temperature matrix is below, with boundary conditions 3.12-15 (described above) shown at the appropriate points. The “x’s” denote a Dirichlet condition, while the triangles denote Neumann conditions. For the example in Figure 3.1, a constant wall temperature case is shown. Each internal node is prescribed with an individual (singular) subscript for labeling in the code. The labeling scheme corresponds to the relationship described in equation 3.28 between \( k \) (the index number) and the respective axial and radial grid location indices \( i \) and \( j \) (Stanoyevitch, 2005).

\[ k = i + N(M - j) \] (3.28)

where \( N \) is the number is axial grid points and \( M \) is the number of radial grid points.
Equations 3.12-3.14 describe the gradient form of the boundary conditions. Because the central differencing scheme cannot be directly applied at the boundaries, one method of boundary definitions is to implement a forward differencing scheme at the left and bottom edge nodes and a backward differencing scheme at the right and top (Stanoyevitch, 2005). Although this method is not as accurate as the central differencing approach, forward and backward differencing allows full definition of the boundaries, and can be used for the studied parabolic problem. Mesh density will be a key factor in enabling these schemes to define the tube boundaries. The current study employs a second-order backward finite
difference at the Neumann boundaries described in equations 3.13-3.14 to increase stability and accuracy at those locations (Stanoyevitch, 2005). As an example, the quenched reaction condition from equation 3.13 is represented in the following way:

$$\frac{\partial T}{\partial z}_{|_{nz}} = 0 = \frac{3T_{nz-1,j} - 4T_{nz,j} + T_{nz-2,j}}{2\Delta z} \Rightarrow T_{nz} = \frac{4}{3} T_{nz-1,j} - \frac{1}{3} T_{nz-2,j}$$  (3.29)

The symmetry condition (3.14) is similarly represented by $T_{i,j} = \frac{4}{3} T_{i+1,j} - \frac{1}{3} T_{i,j}$ Equation 3.29 is written for each (i,j) pair combination, totaling 25 for the 5x5 example matrix used in this section, substituting the boundary condition equations above in the appropriate spot in the matrices. The coefficients described in equation 3.26 at the Neumann boundaries need to include the ghost-node correction factors from equation 3.29. The equations are then coded into MATLAB and solved simultaneously. Figure 3.2 is a layout of the full energy matrices for direct inversion, and Figure 3.3 is a flow chart that describes the iterative solution technique used in the current study.
Figure 3.2: Energy matrices for direct inversion
Four iterations of the kinetic subroutine-followed-by- species equation solutions were found to provide a stable composition for transport coefficient calculation. Following 300 full iterations of energy and kinetic/species subroutine solution, the solution was stable and did not significantly change. Thus, the validation and sensitivity studies will employ 300 full-model iterations, each containing four sub-iterations of kinetic/species equation solution.
3.3.3 Validation Plan

The current approach, while having been used in the literature for other applications, must be validated for the steam methane reforming reaction with external heat source. Comparing the predictive results with experimental data is the most accurate and historically accepted validation scheme, and the current work will validate the code for the experimental results presented by Valensa (2009). CFD is a capable analytical tool for predicting transport behavior, and it could also be used to numerically compare the boundary layer-approximated (parabolic) 2-D transport with the full 2-D (elliptic) case, as it includes behaviors and factors that the boundary layer model can only approximate (Raja et al., 2000).

To validate the transport model subroutines, the predictive results are compared with a widely-accepted textbook solution. The energy conservation equation will be solved for the simple problem of convective flow in a tube without diffusion or reaction. The equation will be solved (in matrix form) with the most easily-specified wall boundary condition: constant wall temperature (Dirichlet). The constant temperature solution will also be used to determine the base case mesh size. Because MATLAB contains inherent numerical errors, simply defining an enormous mesh will not provide an accurate solution. As the mesh density becomes increasingly large, the magnitude of the numerical errors (truncation, roundoff, etc.) will begin to exceed that of the analytical error associated with the model assumptions, causing a divergence in the model solution.

The species equations can not be validated in this same manner, as specifying a constant wall concentration would over-constrain the problem and violate conservation of mass. It is reasonable to infer that implementing the matrix inversion technique used in the
energy equation to the species equations will enable the model to predict accurate mass
transport behavior. Sherwood number is expected to be close in magnitude to Nusselt
number (Gupta and Balakotaiah, 2001), with the discrepancy found in differences between
the Schmidt and Prandtl numbers. Finally, the reaction kinetics and methane conversion can
be compared and tuned to the experimental results of a kinetic calibration test program,
described in section 3.3.4.

The validated transport models can now be used to solve the simplified conservation
equations according to the given boundary conditions with an external heat source. The
analysis will be conducted for flow in a round tube, and will be compared experimental
results for the same GHSV.

3.3.4 Experimental Testing Description

A test unit was built to calibrate the reaction model. The reactor depicted in Figure
1.5 was fabricated for ease of temperature and composition measurement at various points
along the reacting flow length. The outer fin of the reactor was dip-coated with the same
coating as the calibration sample. The coated reactor is shown in Figure 3.4.
Figure 3.4: Cylinder with brazed fins coated with precious metal catalyst (Valensa, 2009).

The reactor fin was made of a Fecralloy® material primarily comprised of iron, chromium and aluminum. Prior to the dip coating process, the brazed cylinder underwent a pre-oxidation cycle (~900°C exposure for about 4 hours) to form aluminum-oxide on the surface of the Fecralloy material. The aluminum oxide provides a rough surface on the fin surface, which facilitates coating with an alumina/ceria washcoat, the carrying mechanism for the precious metal catalyst particles. The precious metal catalyst blend is proprietary to the catalyst supplier, but is likely comprised of rhodium, platinum and/or palladium (Heck and Farrauto, 2002).

The coated reactor was then installed into the full test unit, shown in Figure 3.5, which contained both temperature measurement ports and gas sampling ports along the reactor length.
The ports were placed in various locations around the circumference of the reactor to ascertain circumferential thermal and compositional distribution. The temperature ports bracketed the reacting fin so that the first and last ports provided, respectively, the inlet and outlet temperature of the reactor fin in the flow direction. Temperatures were measured with 1.5mm diameter Omega K-type mineral-insulated thermocouples with stainless steel sheaths. The thermocouples were fed through Swagelok compression fittings (shown in Figure 3.5 with black caps), and the temperatures were measured to an accuracy of +/- 2%. The gas sample ports were located as close to the temperature ports as possible to provide composition information with respect to radial temperature distribution.
Figure 3.6 shows a flow diagram schematic of the internals of the test unit. “A” and “B” represent the respective steam/methane mixed fuel inlet and reformate (comprised of H₂, CO₂, CO, H₂O and CH₄) outlet fittings; the reacting fluid passes through the blue fin, which is coated with catalyst. “C” and “D” represent the respective fuel cell exhaust inlet and outlet, oriented in counterflow flow direction with the reacting fluid. An internal baffle, depicted by the dashed lines in Figure 3.6, directs the exhaust flow through the center of the unit to the far right as shown in the figure, and following a 180° turn, routes the exhaust flow through the red (uncoated) fin to provide heat to the reaction.
Table 3.2 describes the cylinder and fin geometry and material used in the reactor only test unit in Figure 3.5. The six gas sample ports were made of 3.2mm OD UNS N06600 material.

<table>
<thead>
<tr>
<th>Cylinders (color/location in Fig. 3.6)</th>
<th>OD (mm)</th>
<th>Wall thickness (mm)</th>
<th>Material UNS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (green)</td>
<td>82.6</td>
<td>1.24</td>
<td>N06601</td>
</tr>
<tr>
<td>Outer shell (gray at exterior of unit)</td>
<td>95.3</td>
<td>1.65</td>
<td>N06601</td>
</tr>
<tr>
<td>Baffle (dashed near reactor)</td>
<td>66.2</td>
<td>1.24</td>
<td>N08810/11</td>
</tr>
<tr>
<td>Exhaust inlet (dashed near point C)</td>
<td>25.4</td>
<td>1.65</td>
<td>N08810/11</td>
</tr>
<tr>
<td>Exhaust outlet (yellow around inlet)</td>
<td>38.1</td>
<td>0.94</td>
<td>N08810/11</td>
</tr>
<tr>
<td>Exhaust outlet stub (yellow near D)</td>
<td>25.4</td>
<td>0.94</td>
<td>N08810/11</td>
</tr>
<tr>
<td>Mixed fuel inlet (gray at A)</td>
<td>12.7</td>
<td>0.94</td>
<td>N06601</td>
</tr>
<tr>
<td>Reformate outlet (gray near B)</td>
<td>12.7</td>
<td>0.94</td>
<td>N06601</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fins (color/location in Fig. 3.6)</th>
<th>Flow Length (mm)</th>
<th>Height (mm)</th>
<th>Pitch (mm)</th>
<th>Thickness (mm)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (blue, outer)</td>
<td>140</td>
<td>4.11</td>
<td>1.10</td>
<td>0.15</td>
<td>Fecralloy</td>
</tr>
<tr>
<td>Exhaust (red, inner)</td>
<td>140</td>
<td>6.38</td>
<td>1.34</td>
<td>0.15</td>
<td>N08810/11</td>
</tr>
</tbody>
</table>

Table 3.2: Cylinder and fin geometry and materials in reactor test unit.

The reactor-only test piece was installed into a test stand depicted in Figures 3.7-10. The actual application uses the reformer module in an environment around 500°C, so a Nabertherm Top Hat Kiln furnace hood was used to control the ambient temperature around the test unit (Valensa, 2009). A 6kW Sylvania electric heater was used to heat the “exhaust,” simulated by hot air, entering the reactor. The heater is wrapped in foil and mounted beneath the test unit in Figure 3.7. In addition to the pre-determined blend of steam and methane, the fuel mixture contained a small amount of nitrogen. The constant flow of nitrogen was added to enable gas chromatograph measurement since it does not react. The experimental results were adjusted to consider only reacting constituents. The gas chromatograph in the test stand
is a Varian GC Series gas chromatograph, which measures compositions to within +/- 1%). The flow rates were measured to within accuracies of +/- 2%. Steam, which is mixed with the methane to provide the reacting fluid, was generated with de-ionized water in an external coil that was wrapped around the exhaust of the test unit beneath the furnace hood (denoted by the arrow in Figure 3.9).

Figure 3.7: Test stand for reactor performance validation test (Valensa, 2009).
Figure 3.8: Reactor/heat exchanger installed in the test stand (Valensa, 2009).

Figure 3.9: Steam generation coil around the exhaust outlet tube (Valensa, 2009).
Two different fuel mixtures, defined by steam-to-carbon ratio (S:C), were run through the unit for reactor performance testing. Data was collected following achievement of stable system operation at constant flow rates and temperatures. The fuel mixtures tested were: S:C=2.5 and 3.0, providing at least a 25% safety margin of excess steam was present to prevent coking of the methane. Carbon coke is formed on the metal surfaces at temperatures exceeding 600°C at S:C ratios below 2.0 (Larminie and Dicks, 2000). Beyond S:C=3.0, the hot-coil steam generation method employed by the test stand was unable to provide stable operation due to the increased heat required to vaporize the steam (Valensa, 2009). This instability is typically seen as a pressure fluctuation, which could vary the composition of the reformed fuel entering the downstream system components. The respective experimental
GHSV’s were 4650 hr\(^{-1}\) and 5300 hr\(^{-1}\), which provides the basis for the tube size and flow rates selected in this thesis.

### 3.3.5 Approach Justification

To justify the approach presented in the current study, a study by Raja et al. (2000) is used to compare the 1-D plug flow, the 2-D convection-diffusion boundary layer and the 2-D Navier-Stokes models. Their paper states that with increasing Reynold’s number, the boundary layer assumptions are increasingly valid. Although the current work is entirely in the laminar flow regime, the Raja study states that at Reynold’s numbers above 200, radial diffusion and convective transport dominate diffusive transport. This work operates entirely in Reynold’s ranges above 200, in support of using the boundary layer assumptions for the analysis. Because the diffusive transport is not dominant in the scope of this analysis, the second-order terms in \(z\) can be eliminated, as stated previously. This simplification changes the character of the equations from elliptical to parabolic, greatly reducing the degree of computational complexity of the solution matrices.

The authors state that the primary difference between the boundary layer equations and the Navier-Stokes model is that the species mass fraction contours are more evenly spaced in the Navier-Stokes case. Neglecting axial diffusion in the boundary layer model is thought to be the primary explanation for this phenomenon. Figures 3.11-12 below illustrate this trend:
Figure 3.11: Comparison of the CH₄ mass fraction contour maps for the Navier-Stokes (lower panels) and boundary-layer (upper panels) models. The upper channel shows $Re_p=200$ case and the lower channel shows a $Re_p=2000$ case. For visual clarity, the radial coordinate has been multiplied by a factor of 20. This actual disparity is not as severe as the figure suggests (Raja et al., 2000).

Figure 3.12: Comparison of the CO₂ mass fraction contour maps for the Navier-Stokes (lower panels) and boundary-layer (upper panels) models. The upper channel shows $Re_p=200$ case and the lower channel shows a $Re_p=2000$ case. For visual clarity, the radial coordinate has been multiplied by a factor of 20. This actual disparity is not as severe as the figure suggests (Raja et al., 2000).
The plug-flow model lumps the radial diffusion effects into a factor to approximate two-dimensional flow. Because this approach neglects the species boundary layer, the plug-flow model predicts accelerated fuel consumption and subsequent conversion to products. The images below depict this behavior of the 1-D model, and compare it with the other two models at Reynolds numbers of 200 and 2000, respectively. The plug-flow model symbolized by “Plug,” while the boundary layer approach is called “B-L” and the 3-D Navier-Stokes is shown as “N-S.” These plots represent the methane combustion reaction, but this thesis assumes that the trends in Figures 3.11-14 should be valid for the currently-studied SMR reaction mechanism.

Figure 3.13: Axial profiles of the mass-averaged CH₄, H₂O and CO₂ mass fractions at Reₐ=200 (Raja et al., 2000)
Clearly, the plug-flow model overpredicts the conversion due to the neglect of radial diffusion. An interesting trend is shown by the comparison of the boundary layer model and the Navier-Stokes model. Raja et al. state that the boundary layer approach is more applicable at “higher” Reynolds numbers, but the study considers 200 to be an appropriate range. The current analysis utilizes Reynolds’s numbers on the order of 200, so the approach is valid for the flow rates in this study. At that value, shown from Figure 3.13, the boundary layer model nearly matches the Navier-Stokes model, with small disparities attributed to the boundary layer’s neglect of axial diffusion. Looking at the compositions at a Reynolds’s number of 2000, it is worth eliminating axial diffusion in order to decrease the model’s computational complexity for all laminar flow cases. Furthermore, Raja et al. conclude that the boundary layer approach is increasingly valid for kinetically limited cases (low Damköhler number). The authors’ stated applicability range for the boundary layer approach
is for the channel diameter-to-length ratio of much less than the Reynolds’s number. For the current case, the \( \frac{d}{L} \) ratio 0.02 with \( 100 < \text{Re}_d < 1000 \), suggesting the boundary layer assumptions should be valid.

A 1996 study by Bazhlekov, Koleva and Vasileva used the tridiagonal matrix algorithm (TDMA) to solve the 2-D convection-diffusion equations with chemical reaction in two phases, using the boundary layer assumptions for flow through a flat interface. The equation system is linearized and discretized, and the results are compared with existing theoretical results at different parameter values.

The authors added terms in the interface boundary condition expressions, but the principle solution method is finite difference. Central, upwinding and conservative differencing approaches are presented, with little variation was seen between the central and upwinding methods (Bazhlekov, Koleva and Vasileva, 1996). The central and upwinding schemes require a smaller marching step than the conservative method, especially near the origin. In general, the study verified the predictive accuracy of the approach methodology when compared with historical theoretical results. Table 3.3 shows the results of the integral of the y-direction concentration gradient \( I_1 = \int_0^1 \left( \frac{\partial C}{\partial y_1} \right)_{y_1=0} dx \) are presented for the three solution schemes, and can be compared with the asymptotic theory solution \( I_1 = 0.45547 \) for \( D_a=0 \) (kinetically-limited reaction):
Table 3.3: \( \omega \) values at \( Da=0 \). (40) refers to the upwinding difference scheme, (39) is the central difference method and (42) is the conservative difference method. \( \omega^n \) represents a specific mesh density (Bazhlekov et al., 1996)

<table>
<thead>
<tr>
<th>( \omega )</th>
<th>Approximation of (29) with (40)</th>
<th>Approximation of (29) with (39)</th>
<th>Approximation of (29) with (42)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega^{00} )</td>
<td>0.43445</td>
<td>0.43545</td>
<td>0.45462</td>
</tr>
<tr>
<td>( \omega^{01} )</td>
<td>0.43512</td>
<td>0.43562</td>
<td>0.45508</td>
</tr>
<tr>
<td>( \omega^{02} )</td>
<td>0.43547</td>
<td>0.43573</td>
<td>0.45529</td>
</tr>
<tr>
<td>( \omega^{03} )</td>
<td>0.43565</td>
<td>0.43579</td>
<td>0.45540</td>
</tr>
<tr>
<td>( \omega^{04} )</td>
<td>0.43574</td>
<td>0.43581</td>
<td>0.45544</td>
</tr>
</tbody>
</table>

To a degree, the accuracy of the results is determined by the mesh density. A point of diminishing return can be reached, however, which only increases the degree of computational intensity. The conservative scheme, (42), is the least dependent on mesh density, and predicts the historical result with the most precision of the three methods at less than 0.02% difference (Bazhlekov et al., 1996). The authors cite a smaller time step at the origin as a potential improvement to the broad predictive ability of both the upwinding and the central differencing schemes. Stability challenges are the likely failure mode for the predictions. The current study utilizes a fully-implicit finite difference scheme, similar to that of the Crank-Nicolson method, and has decreased stability concerns due to second-order nature of stability. This method is expected to be stable for all points of the full-model case described in section 4.4, and should be less dependent on mesh density than other implicit schemes, such as Crank-Nicholson, as all four boundary conditions are explicitly defined.
3.4 Application of Catalytic Minichannel Reactor

Once the approach has been validated according to the steps described in the previous section, the model will be run for the desired finned-cylinder conditions, with the GHSV through one finned channel matching the GHSV through a round tube. The representative mass flow rate of mixed methane and steam become 0.03504 g/s for a steam-to-carbon ratio of 2.5 and 0.04288 g/s for S:C=3.0. The curves of species molar flow vs. axial position for both cases will be presented to show the direct comparison between the 2-D boundary layer model and the experimental data discussed in section 4.3.

The transport coefficients will be derived from the wall temperature values per the discretized equations at a single methane and steam mixture flow rate. There will be one correlation for Nusselt number, and five Sherwood correlations, one for each represented species in the reaction mechanism. The baseline case will not account for washcoat diffusion, but will include the critical radial diffusion in the bulk fluid. A future study may be to investigate the impact of washcoat diffusion, but for thin washcoats (~100 µm), this effect should not have a significant impact (Hayes, Kolaczkowski and Thomas, 1992, Raja et al., 2000).
3.5 Novelty of the Current Research

The novelty of the boundary layer model for convection-diffusion transport in a catalytic finned reactor can be seen in the following categories:

- Improved wall boundary condition (described in section 3.1.2)
  - Variable wall-temperature from highly-endothermic reaction
  - Includes concentration/temperature gradients in two directions
  - Does not require the large degree of computational capacity of CFD
- Non-isothermal low-pressure SMR reaction
  - More accurately simulates reaction conditions of a reaction that has not been extensively modeled in the literature
- Reactor geometry with complex boundary conditions used to derive position, Reynolds’ and Prandtl/Schmidt-dependent transport coefficients
  - Improves local model predictability over entire length
  - Enables rapid evaluation of reactor kinetic performance with gas-phase diffusion
- More accurate description of the interaction of transport with SMR reaction kinetics than prior 2-D reactor models from inclusion of transport and kinetic property variation with both axial and radial position
- Potential to apply coefficients to an industrially-present geometry demonstrates the market pull for improved, efficient predictability of convection-diffusion coupled with reaction
As mentioned in Section 3.3.2, the wall boundary condition includes an external heat source through implementation of a varying-temperature profile, eliminating the often-used adiabatic channel boundary condition, which is not observed in practice. From conclusions drawn in the literature, accurately defining the boundary condition at the wall is a major first step toward formulating a useful model. Because the SMR and WGS reactions are (respectively) endo- and exothermic, neglecting heat exchange into and out of the channel may provide erroneous results. In reality, the heat input from the source has a direct and profound impact on the methane conversion and reformate outlet temperature.

The non-isothermal reaction, using the Xu and Froment kinetic mechanism for steam methane reforming (1989a-b), more accurately describes the physical intra-channel reactor conditions seen in practical application than other models. Position-dependent coefficients, which have not been extensively investigated in the literature, are derived from the reactor geometry to facilitate better local model predictability over the entire reactor length than prior models. Finally, the model provides a more accurate description of the interaction of convective transport with reaction at the reaction temperature than prior models due to the inclusion of radial concentration and temperature gradients, and radial diffusion of reacting species toward the channel wall. As a result, the current work aims to provide the accuracy of the higher-order CFD models while maintaining a low level of computational complexity and decreased solution time.
4. COMPUTATIONAL MODEL RESULTS

4.1 Validation Studies

Validation studies for both the bulk mean fluid temperature and the Nusselt number for flow through a round tube with a constant wall temperature can also be used to preliminarily determine the efficiency of the mesh size. Raja et al. (2000) implemented 30 radial steps for their boundary layer model, with at least 300 axial mesh points as determined by the method of lines procedure. The Raja group’s grid utilized a variable mesh, however, which the current study aims to avoid for simplicity. Furthermore, MATLAB is not capable of directly inverting a 300x30 matrix for the current model. As a result, the grid dimensions for this study were initially evaluated at axial and radial steps around, respectively, 100 and 30 to ensure the matrices can be solved with relatively minimal computational complexity. A grid size optimization study was performed, with results presented in Appendix B. The initial conclusion was that the optimal grid size is 100x40, with the number of radial steps having the biggest impact on the fully-developed region and the number of axial steps having the greatest effect at the tube inlet region. This relationship will be described in detail in Section 4.2.1.

4.1.1 Mean Temperature Validation

The calculation methodology for analytical bulk mean temperature, used to calculate Nusselt number, was taken from Kays, et al. (2005) for a straight tube. Using the axial
position along the tube, the tube diameter and the constant wall temperature, the mean
temperature can be determined. The mass-averaged bulk mean temperature, calculated from
equation 3.16, is plotted against channel length in Figure 4.1. Thermophysical properties
used to calculate transport coefficients are evaluated at the film temperature (Kays, Crawford
and Weigand, 2005).

![Graph showing bulk mean temperature vs. channel length](image)

**Figure 4.1:** Bulk mean temperature vs. axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and a 100x40 grid size. Re~150, Pr~0.5.

Excellent agreement is seen in the comparison of the mean temperatures from Figure
4.1, with differences not exceeding 2% for the mass-averaged case, even at the channel inlet.
A 100x40 grid was used; section 4.1.2 provides increased confidence in that radial step size,
and it also demonstrates the optimal grid that can be used for computational efficiency while
maintaining predictive accuracy. The axial step size may be decreased with nearly
transparent impact on the fully-developed region. The bulk mean fluid temperature does not change with mesh density for a nearly-constant cell size.

### 4.1.2 Energy Equation Validation

For the current work, Figure 4.2 illustrates the similarity in temperature contour plots between the 100x40 grid and the 200x40 grid, supporting the conclusion that accuracy is not compromised at the coarser of the two grid sizes.

![Temperature Contour Plots](image)

**Figure 4.2:** Contour temperature plot comparison for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5; 100x40 grid (a) and 200x40 grid (b). Re~150, Pr~0.5.

For laminar flow for tube flow with Reynolds’s numbers around 150, the entrance length for the studied tube should be about 0.1 m (z/dₜ=10), according to the equation
\[
\frac{Z_{\text{th.entry}}}{d_h} \approx 0.05\text{RePr} \quad (\text{Kays, Crawford and Weigand, 2005}); \text{ the model is predicting this behavior nearly exactly.}
\]

For the plots in Figures B.1-3, the asymptotic value of the Nusselt number is at most 1.3% above the theoretical value of 3.66 (Incropera & Dewitt, 2002). The primary deviation is seen at the tube inlet, where the Nusselt number is the highest. The accuracy of the prediction of the steep gradient is dependent on and axial grid spacing, especially at the tube entrance. The figures also show that the asymptotic Nusselt number is independent of the number of axial steps for a constant, coarse grid. The slight deviation from analytical asymptotic Nusselt can easily be explained by any propagating rounding errors due to temperature-dependent property inaccuracies, or simply slight numerical discrepancies. As a result of the above-mentioned studies, a grid size of 100x40 appears reasonable to carry forward to the full model (0.8% deviation from analytical Nu value).

### 4.2 Numerical Model Validation

The transport solution methodology can be validated by the energy conservation equation independently to determine the validity and accuracy of the solution. Applying the constant wall temperature boundary condition to the energy equation, while neglecting any heat generation from chemical reaction, provides a temperature profile throughout the tube that can be translated into a dimensionless, local wall transport correlation. The profile can then be compared to the known text book solution for the current geometry, fully-developed.
laminar flow in a tube from Chapter 8 of Kays, et al. (2005). The process by which the Nusselt and Sherwood correlations are calculated can be broken down into three steps:

- Solution of transport and kinetic model equations to obtain local temperature and concentration profiles for the bulk mean fluid locations along the tube axis at the constant wall temperature/concentration boundary condition
- The resulting bulk fluid temperatures and concentrations are then used to compute the respective local heat and mass transfer coefficients at the channel wall
- Using the film conductivity and diffusivity and the hydraulic diameter as the characteristic length, the local wall Nusselt and Sherwood numbers are calculated and correlated as a function of relevant parameters, such as normalized axial position ($z/d_h$), Reynold’s number, Prandtl/Schmidt number and/or inverse Graetz number as described by equation 4.3 (Raja et al., 2000)

The simplified energy conservation models can be solved independently at the conditions of the textbook case, and their results can be plotted with the textbook results for comparison and transport model validation. The kinetics will also be validated using a plug-flow model for approach application verification and experimental data from an isothermal calibration run (Valensa, 2009). The initial grid size will be 100x40, as determined in section 4.1.
4.2.1 Constant Wall Temperature Boundary Validation

For the constant wall temperature/concentration condition, Eq. 1.9 is applicable, since the surface temperature is constant along the tube length. Newton’s Law of Cooling \( q'' = h(T_w - T_m) \) and its analogous mass transfer relation \( j_A'' = h_{mass}(\rho_{A,w} - \rho_{A,m}) \) can be directly implemented along the axis for the constant wall temperature. For the currently-studied tube geometry, the convective heat transfer coefficients for flow through a round tube with a constant wall temperature can be derived from the Nusselt values provided in Kays, et al. (shown in table 4.1), according to equation 4.1.

<table>
<thead>
<tr>
<th>z[mm]</th>
<th>z/d_h []</th>
<th>Gz^{-1} []</th>
<th>T_m [K]</th>
<th>h [W/m^2-K]</th>
<th>Nu []</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>12.8</td>
</tr>
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<td>0.002</td>
<td>0.233</td>
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<td>0.582</td>
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<td>870</td>
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</tr>
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<td>50</td>
<td>0.43</td>
<td>948</td>
<td>58.4</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Table 4.1: Analytical parameters for flow through a round tube with a constant wall temperature (Kays, Crawford and Weigand, 2005), and calculated analytical \( T_m \) and \( h \) values based on fluid property data.

\[
h(z, R) = \frac{Nu \cdot k_{film}(z)}{d_h} \tag{4.1}
\]

Per the approach of Raja et al. (2000), the Nusselt and Sherwood numbers are calculated by computing the convective transfer coefficients, implementing the bulk temperature/density profiles described in section 4.1.1 and using a mass-averaged density for
both total, the Nusselt and Sherwood correlations in equation 1.10 can be determined for each axial grid point.

The Raja group concluded that the Sherwood number should be between 1 and 6 following the high values seen in the immediate vicinity of the tube entrance and be similar in asymptotic magnitude to the Nusselt number. The shapes of the curves may be different, however, due to differences in thermal and mass diffusion coefficient and Sherwood numbers. As stated above, it is not possible to validate the constant-wall concentration Sherwood number as mass conservation would be violated. Nusselt number is plotted against normalized axial length and compared with the analytical value in Figure 4.3.

![Figure 4.3: Nusselt number vs. normalized axial length, S:C=2.5, grid sizes 40x40 and 100x40.](image)

As stated above, there is a deviation to the Nusselt curves at the immediate inlet of the tube, likely due to the coarseness of the mesh at that location. The figure confirms that a 40x40 grid is sufficient for this study, especially considering the multiple iterations that are
planned for the full model. The fully-developed value of Nusselt number for the 40x40 (and the 100x40) grids within about 1% of the theoretical value. Figure 4.3 also confirms the conclusion that the asymptotic (or fully-developed) transport coefficient is most strongly affected by the radial grid spacing, while the inlet region is most strongly influenced by axial grid spacing. Further refinement of the mesh with a constant cell size would improve the results at the inlet, but the available memory for solution would likely be exceeded before the analytical inlet profile could be modeled (please see Appendix B for grid-size sensitivity study). The flat profile reflects constant properties; the variable properties included in the full model should provide an upward slope to the transport plots in the fully-developed flow regime. Assigning a variable mesh both the reactor inlet in the axial direction and wall in the radial direction, however, would improve the predictive capability of the model, especially at the inlet without unnecessarily burdening the system memory. Implementing a variable mesh scheme in that fashion would likely require a different solution technique, and could be the subject of a future study.

As concluded by the Gupta and Balakotaiah study (2001), the Nusselt number for the constant wall temperature case in Figure 4.3 exhibits asymptotic behavior following full development of thermal boundary layers. Due to the [initially] fully-developed hydrodynamic flow assumption, any entry effects seen in a plot of the local Nusselt/Sherwood number along the tube flow length are attributed to the thermal boundary layer (Hayes and Kolaczkowski, 1999). It should be noted that although the velocity profile is parabolic due to the fully-developed hydrodynamic flow assumption, mass conservation is
preserved by updating the density in the mean velocity (equation 3.11b), which causes the velocity profile to change due to changes in density.

4.2.2 Isothermal Reaction Kinetics Model Validation

The primary outcome of this thesis is to determine the dimensionless temperature and concentration gradients for a given reaction scheme in a specified geometry. Gas Hourly Space Velocity (GHSV) is determined by the catalyst type to ensure that sufficient contact area and residence time exists for the reacting flow in the presence of catalyst, so that to the desired conversion can ultimately be achieved. GHSV represents the ratio of volumetric reactant flow to reactor volume, with units of hr\(^{-1}\). Significant investigation has been done by the catalyst supply base to determine appropriate space velocities for the SMR reaction through a round tube.

The reaction kinetics model can be validated with isothermal kinetics calibration testing, as described in the Valenza study (2009). The calibration testing was conducted at varying values of GHSV at 600°C, 650°C and 700°C. The target S:C was 2.5, but the ratio varied between 2.3-2.5 due to water control issues. The aim was to increase the GHSV to achieve the point at which equilibrium methane conversion could no longer be reached; however this point was never able to be achieved due to capacity limitations in the water vaporizer. A gas chromatograph (GC) was used to measure the product compositions, which necessitated a constant flow of nitrogen (18 mass percent at 5000 hr\(^{-1}\) GHSV point) to be added to the mixed steam/methane stream for flow stability. The addition of nitrogen is
especially influential at low GHSV values (< 7000 hr\(^{-1}\)), since the partial pressure of nitrogen increases with decreased flow rates of reactants for the same volume. Operating at low pressures artificially elevates the equilibrium methane conversion due to the presence of nitrogen (Valensa, 2009). The experimental data used to validate the model has been adjusted to discount nitrogen from the partial pressures (Valensa, 2009). Figure 4.4 is a picture of the 60 mm x 60 mm sample used to validate the reaction model.

Since this study is aimed at including radial diffusion in a 2-D model and not kinetic model development, the catalyst effectiveness factor introduced in the Valensa study, \( \eta \) in equation 3.15, was used in this work. This factor accounts for the disparity between the Xu and Froment (XF) kinetic mechanism, developed for nickel catalyst, and the precious metal
catalyst used for the calibration testing. The metric used for comparing the kinetic model in
the MATLAB code to the Valensa study was methane conversion. The catalyst factor used
in the Valensa study ($\eta=15$) was developed using a plug-flow model. Since the conversions
are solved by averaging the radial molar compositions that vary due to inclusion of diffusive
effects, the new catalyst factor, determined to be 12 for both S:C=2.5 and S:C=3.0, was
found by applying catalyst factors of 4, 8 and 12 to the full model. The impact of each
catalyst effectiveness factor on Sherwood number is discussed in Appendix section B.2.

Figure 4.5 shows the methane conversion results from the isothermal calibration
testing referenced above.

![Figure 4.5: Methane conversion results from isothermal kinetics calibration testing (Valensa, 2009).](image)
Figure 4.6 is a parity plot of numerical methane conversions at different catalyst effectiveness factors vs. experimental results. Through this plot, a catalyst factor of 12 is shown to best fit the data with the best precision of the three points investigated.

Figure 4.6: Parity plot of methane conversion. 40x40 grid; S:C=2.5; η=4, 8 and 12.

Figure 4.6 confirms that the selected Xu and Froment LHHW model agreed well with the test data following correlation. The catalyst bed density was taken to be a constant value, 3.5 g catalyst/L for both the kinetic calibration model and full model (Valensa, 2009). Catalyst factors of 8 and 12 slightly over predict the conversion at lower temperatures in the isothermal tests. Due to the lower-temperature fuel inlet in the full model and the increased resistance due to thermal diffusion, the highest catalyst factor of the three in Figure 4.6, 12, was selected for the full model. A constant flow of nitrogen was added to the model to replicate the experiment, which used nitrogen to enable gas chromatograph measurement by
providing a calibration standard that can be converted to moles at any point along the reactor length. A significant amount of nitrogen will influence the partial pressures, conversion extents and diffusion rates of the reacting gases, despite its inert reaction behavior. The mass flow of nitrogen, nearly 20 mass percent at 5000 hr⁻¹ in the calibration sample, is 1.7% in the full model. This small amount of nitrogen is not expected to affect the results, and was ignored in the full model. Using a catalyst effectiveness factor of 12, the methane conversions at each fuel mixture ratio are plotted in Figures 4.7-8.

4.3 Effect of Radial Diffusion on Reactor Performance

The impact of diffusion can be seen in both the methane conversion and molar flow rate variables for a given reaction. Previous simplified models have assumed instantaneous diffusion between the bulk fluid and the reaction site, ignoring a significant transport effect; axial diffusion has historically been ignored. Prior research has described the negligence of radial diffusion as an overprediction of reactor conversion (Raja et al., 2000). The performance metric of methane conversion (which is the fraction of incoming methane converted to desired reaction products) can be used to validate this conclusion for SMR reactions.

The non-isothermal experimental data described in the Valensa study (2009) was used to assess the predictive capability of the numerical 2-D boundary layer model. Using the transport and kinetic model subroutines validated in section 4.2.2 and the 40x40 grid determined in Section 4.2.1, the full model was run at two different steam-to-carbon ratios, 2.5 and 3.0. Channel mass flow rates were defined by matching the GHSV of the full reactor
with the decreased flow area in the channel. Methane conversion for the comparable flow rate was determined in the 2-D model and compared to that of the experimental unit containing the full annular finned reactor. Figure 4.7 illustrates the comparison between the experimental and corrected numerical methane conversion at the two tested fuel mixtures. Element conservation errors were found in analysis of the experimental data, likely due to an under-sampling of hydrogen. The experimental values used in this study were adjusted by increasing the hydrogen flow until the element conservation errors disappeared (Valensa, 2009). The numerical conversions were determined by using bulk-fluid mass-averaged concentrations to account for the total fluid that contains a radial gradient.
Figure 4.7 shows good agreement between the model and experimental data, still with a slight overprediction at 25% reactor length. This trend is likely due excessive kinetics predicted by a coarse mesh at the reactor inlet. The overall shape of the curve matches well with the experimental data, and enables definition of an accurate reactor size. Application of
the methane (and corresponding carbon dioxide) conversions of the 2-D boundary layer model to the full flow rates seen in the experimental apparatus enables direct comparison of the molar flow rates between the numerical and experimental data. The relation of CH$_4$ and CO$_2$ conversion to molar flow rate is described by Xu and Froment (1989a-b). The molar flow rates plotted in Figure 4.8 illustrate a comparison of the compositional breakdown of the reacting flow between the experimental data and the numerical 2-D boundary layer model. Slight discrepancies exist in the hydrogen and steam molar flow curves, but experimental error coupled with numerical approximation are the likely sources of the small deviation of the model to the data.
Figure 4.8: Experimental and normalized numerical molar flows vs. axial position. 40x40 grid; S:C=2.5 (a) and 3.0 (b).

As expected, Figure 4.8 again shows good agreement between the experiment and model prediction. This similarity results from the good conversion agreement shown in Figure 4.7. The steam molar flow rate was the only constituent not measured; it was found by calculating the imbalance in oxygen atoms of the remaining constituents and assuming that the entire amount of the discrepancy existed as steam. Another trend providing confidence in the
model’s predictive capability is that CO and CO₂ cross in the near the end of the reactor tube. This is due to the excessive reaction kinetics near the reactor entrance that encourages the SMR reaction (CO production) and discourages the WGS reaction (CO₂ production). The model predicts this crossing earlier in the flow path than the data suggests, but the flow rates are so similar that a small difference in species flow rate magnitude could create an early crossing of the two streams.

4.4 Non-Adiabatic Heat and Mass Transfer Coefficient Correlations

The validation runs in sections 4.1-3 can be combined for the desired application of developing heat and mass transport coefficient correlations for non-adiabatic flow through a tube with wall reaction, including radial diffusion effects. Using the constant wall temperature/concentration boundary condition, a 40x40 grid with 300 full iterations was used to solve the transport and kinetic equations from which the transport coefficients are derived. The pseudo-constant wall temperature/concentration condition was prescribed (by the method described in Chapter 3) in the form of experimental temperature profiles for each of the fuel mixtures tested to include the effects of reaction rates, heats of reaction and an external heat source.

Hayes and Kolaczkowski (1999) determined Sherwood correlations for heterogeneous methane oxidation for the cases of constant gas-phase wall composition and constant reaction rate. For the current study, neither of these scenarios is valid, and as such there are no analytical Sherwood correlations as a function of inverse Graetz number (or its included parameters) in the literature. The inverse Graetz number equations used in the
Nusselt and methane Sherwood number correlations are shown below in equation 4.2. The Schmidt number, \( \text{Sc} \), is found by dividing the kinematic viscosity of the total fluid by the individual constituent diffusion coefficient (Raja et al., 2000).

\[
G z^{-1} (z) = \frac{z/d_h}{Re_d \text{Pr}} \\
G z_{\text{ch}4}^{-1} (z) = \frac{z/d_h}{Re_d \text{Sc}_{\text{ch}4}}
\]

\[(4.2)\]

It is a common assumption to presume that the correlation for Nusselt number is the same as that of the Sherwood number. This is true to some extent, but only under conditions as described in Bird, Steward and Lightfoot (2002):

1. Constant thermophysical properties
2. Small net mass transfer rates
3. No chemical reaction
4. No viscous dissipation heating
5. No absorption or emission of radiant energy
6. No pressure, thermal or forced diffusion.

Because these conditions are not all true for the current study, it is not expected that the Nusselt number will match the Sherwood number after substituting the analogous parameters (Schmidt number for Prandtl number, mass diffusivity for thermal conductivity) (Raja et al., 2000).
The constituent Sherwood numbers should slightly differ from each other due to variations in constituent density. The inlet region of the reactor is kinetically-limited, due to both the relatively low reforming temperature at the inlet (~415°C) and the abundance of primary fuel constituents \( \text{CH}_4 \) and \( \text{H}_2\text{O} \). Factors that contribute to the Sherwood number curve shape, sign, and/or absolute value are:

- Fuel mixture ratio
- Reaction mechanism (constituent molecular weights are critical factors in determining the local mixture density, which, in combination with the mass-averaged bulk fluid density, is used to calculate the Sherwood numbers)
- Coarseness of the grid, leading to large differences between reacting wall density and that of the adjacent cells
- Catalyst effectiveness factor, which alters the rates and affects the wall concentrations
- Low-pressure, high temperature flow conditions, yielding densities and density changes that are on the order of the axial step size

The constituents only present as products in reactions R1, R2 and R4 (CO\(_2\) and H\(_2\)) are most sensitive to the catalyst effectiveness factor. A catalyst factor of 12 was shown to match the non-isothermal experimental methane conversion results in Figure 4.7-8; however, applying this value led to decreased stability in the carbon dioxide and hydrogen Sherwood numbers. The same conditions were run for a catalyst factor of 1 for comparison. All five Sherwood numbers for a catalyst factor of 1 were plotted against the methane, steam and
carbon monoxide Sherwood curves for a catalyst factor of 12. The comparison is shown in Figure 4.9.

From Figure 4.9, the average difference at each point along the Sherwood curve for CH$_4$, H$_2$O and CO is less than 2%. The design of a reactor typically includes catalyst-life degradation factor on the order of 10-15% or more to ensure performance throughout the product life; the 2% disparity due to catalyst factor is easily absorbed by that factor. As a result, the catalyst factor should only be used to determine the reactor methane conversion, not the transport behavior.
Figure 4.10 is plot of the numerically-derived Nusselt and Sherwood curves for the S:C=2.5 and S:C=3.0 cases, which will be used for development of the correlations. The Nusselt and Sherwood curves differ by the reasons given above.

Figure 4.10: Numerical Nusselt and Sherwood number vs. axial position. 40x40 grid; S:C=2.5 (a) and 3.0 (b).
The curvature in all of the transport parameters in the full model can be attributed to the presence of heterogeneous catalytic reaction (Raja, et al., 2000). The highly non-linear nature of the catalytic reaction mechanism employed in this study causes a deviation from the simple monotonic behavior observed in Figure 4.3. Magnitudes vary for the multitude of reasons listed above, and the sign of the Sherwood number indicated whether the constituent flow is traveling to the wall (positive) or away from it (negative).

An investigation of the literature provided the analytical and experimentally-determined correlations to be used for data fitting. The non-adiabatic Nusselt curve (for non-reacting systems) is represented by equation 4.3, taken from Incropera and Dewitt (2002).

\[
\text{Nu} = 3.66 + \frac{0.0668 \left( \frac{d_h}{z} \right) \text{Re}_d \text{Pr}}{1 + 0.04 \left( \frac{d_h}{z} \right) \text{Re}_d \text{Pr}^3} \tag{4.3}
\]

Equation 4.3 provides a simple, monotonic path to the asymptote; however, due to the presence of the reaction at the wall, the Nusselt number exhibits the shape seen in Figure 4.15 (Raja et al., 2000), which eliminates the traditional correlation in equation 4.4 as a possible form.

Correlating the Sherwood curve required additional study, as there are no nearly-universally accepted correlations for straight cylinder geometry (Joshi, Harold and Balakotaiah, 2010). Figure 4.10 illustrates curves from various analytical methane Sherwood
number correlations, along with the numerically-derived curve. A summary of the analytical
curves can be found in Joshi, et al. (2010), with the exception of the WWWR curve as shown
in the legend of Figure 4.10 (in red); that curve is taken from Welty, Wicks, Wilson and

Figure 4.11: Numerical Sherwood number and analytical correlations vs. inverse Graetz number for S:C=2.5. Equations 4,
5, 6, 13 and 14 are given in Joshi et al. (2010), and WWWR is taken from Welty et al. (2001).

Clearly, none of the recent correlations can capture the full behavior of the numerical data
curve, which is similar in shape to the Sherwood numbers in the Raja et al. study (for the
coincident constituents in methane combustion reaction) for Reynold’s numbers around 150.
As a result, the Sherwood number for mass transport with chemical reaction must be pieced
together, as appropriate analytical correlations do not exist in the literature, supporting the
conclusions of Raja et al. (2000) and Hayes and Kolaczkowski (1999). Equation 4.4
provides the form and nomenclature for the polynomial fit. Two polynomial fits comprise the composite transport correlation; the first describes the inlet region (~initial 10% of reactor length) and the second describes the fully-developed region.

Equation 4.4 governs the predicted local wall Nusselt and Sherwood numbers along the axial tube direction, which are determined by a sixth-order polynomial relating inverse Graetz, the independent variable, to Nusselt or Sherwood number, the dependent variable.

\[
\frac{Nu}{Sh} = A\left(\frac{1}{Gz}\right)^6 + B\left(\frac{1}{Gz}\right)^5 + C\left(\frac{1}{Gz}\right)^4 + D\left(\frac{1}{Gz}\right)^3 + E\left(\frac{1}{Gz}\right)^2 + F\left(\frac{1}{Gz}\right) + G \quad (4.4)
\]

Figures 4.12 and 4.13 illustrate the comparison between the respective two-part Nusselt and methane Sherwood number correlations and their numerical solutions at both steam-to-carbon ratios. The figures demonstrate excellent agreement between the numerical and correlated, predicted values. The comparison plots for the remaining four constituents H₂O, CO, CO₂ and H₂ can be found in Appendix C.
Figure 4.12: Numerical Nusselt number vs. 2-part correlation for S:C=2.5 and 3.0.

Figure 4.13: Numerical methane Sherwood number vs. 2-part correlation for S:C=2.5 and 3.0.
Finally, tables 4.3 and 4.4 give the coefficients for equations 4.4 and 4.5, which define the transport correlations for the conditions of this study. Coefficient of determination ($R^2$) values, which would be unity for perfect agreement, vary between 0.9949 and 1 for all cases at both S:C ratios. This coefficient demonstrates accurate prediction of Nusselt and Sherwood number in both accuracy and precision along the entire transport curves.

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Table 4.3: Nusselt and Sherwood number correlation parameters for the inlet and fully-developed regions, S:C=2.5.

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Table 4.4: Nusselt and Sherwood number correlation parameters for the inlet and fully-developed regions, S:C=3.0.
While the correlations have been developed for non-adiabatic SMR, increased effort could be made through experimental study to generate a curve that captures the mass transport behavior for both the inlet and remaining reactor length. A piece-wise function may be sufficient, though, due to the drastic difference in curve shape between the inlet and fully-developed regions. The reaction creates non-homogeneous behavior in the curve, and creates slight differences in the shapes of the individual Sherwood curves.
5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The 2-D boundary layer model with radial diffusion effects and wall reaction accurately predicts the methane conversion for the studied reactions when compared to an empirically-calibrated model for laminar flow through a tube. This study confirms the conclusions of Raja et al. (2000) regarding: the necessity to include radial thermal and mass diffusion on the reaction constituent concentrations and the potential to neglect axial diffusion without sacrificing predictive accuracy. The full model converged in less than 45 minutes for the described solution method in Section 3.3.2 for 40 axial steps and 40 radial steps at 300 full iterations, which is a substantial improvement over complex CFD models for similar reaction schemes and reactor geometries.

For laminar flow, the model demonstrated asymptotic behavior for both Nusselt and Sherwood numbers, which is consistent with the literature (Gupta and Balakotaiah, 2001), though the model curve did not exhibit zero-slope behavior. The model showed that the asymptotic Sherwood numbers for each of the five studied reactant constituents were the same, within about 5%.

Clearly, with coarse meshes, stability and accuracy are of prime concern. The proposed solution technique is but one possible manner in which to solve the problem of coupled convection-diffusion with wall reaction. The model was run for two similar flow rates in a single tube geometry, which is consistent with the aspect ratios (L/dₐ) of existing industrial applications; for robustness, the geometric and reacting flow input parameters may need to be varied to assess the robustness of the model’s predictive capability. Additionally,
stability of the solution, especially with regard to the constant wall flux boundary condition, is difficult to achieve with increased flow rates (Gableman et al., 2005). Therefore, a wall temperature profile must be prescribed to match experimental data in order to achieve an accurate solution if MATLAB is to be used to solve the model.

Using MATLAB with the proposed direct inversion solution technique, described in Sec. 3.3, limits the possible grid size due to the required computational solution time and available memory. Implementing an alternating direction implicit (ADI) scheme, which solves each direction in series, allows the equations for each of the two grid directions to be solved separately. This approach enables smaller matrices to be used, and they can be inverted and solved faster than the full inversion method.

A limitation to the model is that because GHSV (used to determine the flow rate through the tube) is held constant between the application and the model, the application and model fluid velocities may be slightly different, depending on the reacting fluid flow rate and the selected geometry for which the space velocity is matched. This discrepancy could affect the heat transfer characteristics, especially at the reactor inlet, where slight changes in velocity could dramatically affect the heat transfer performance.

The 2-D boundary layer model is intended enable the formulation of heat and mass transfer correlations for the studied reaction, for input into the plug-flow model used in the full system FEA model. These coefficients will improve the predictive capability of the FEA model by incorporating fluid-phase radial diffusive resistance within the plug-flow model (Raja et al., 2000). Simulating 2-D behavior in a 1-D model is the primary application of mass transport correlations in general, and created the need for developing this model.
Additionally, a significant benefit of the developed 2-D boundary layer model is its rapid evaluation of reactor performance, as well as its potential to quickly evaluate the sensitivity of the reactor kinetic and thermal performance to changes in geometry, composition and/or flow rate. The model also contains a separate subroutine for reactor kinetics, so if another reaction mechanism were to be studied, the “KINETICS” subroutine in the 2-D boundary layer model could simply be updated to include the desired mechanism. This would enable the model to be used for a wider range of flow conditions, and potentially different equilibrium reaction mechanisms, such as methanol or higher hydrocarbon (propane, butane, etc.) reforming.

Finally, the model developed in this thesis implements a 20% reduction in catalyst effectiveness factor to the one presented in the Valensa study (2009); as expected, the nickel-based Xu and Froment LHHW kinetic model more accurately predicts the reactor performance for precious metal catalysts when radial diffusion is included. A correction is still needed to account for the improved reaction performance associated with substituting precious metal for nickel. The 2-D model also provides insight as to the impact of precious metal vs. nickel catalyst when compared to the inclusion of radial diffusion. The catalyst factor in the Valensa study includes both diffusion and kinetic mechanism differences. The current study accounts for the transverse diffusion, and due to the fact that the remaining catalyst effectiveness factor is 80% of that determined in Valensa’s study, the performance benefit of a precious metal (likely rhodium) catalyst over nickel is shown to be more significant than the inclusion of radial diffusion. This conclusion may help to scope the priority of future work.
5.2 Recommendations for Future Work

The current approach has demonstrated good predictive capability for solving the transport equations, but there remain opportunities to broaden the range of model’s validity. The model was developed to improve the predictability of the currently-used FEA model; the next step should be to take the transport coefficients derived by the 2-D model and implement them into the plug-flow fluid elements used in the FEA model. This allows 2-D fluid behavior to be included into the complex heat transfer model.

The kinetic model used in the current study is a three-step mechanism proposed by Xu and Froment for SMR kinetics. The third step, the reverse methanation reaction (R4), was included to match experimental data for a different application over a nickel catalyst. Investigation of more detailed chemical mechanisms, such as the Hecht mechanism proposed in Table 1.1, may improve the predictability of the model and, in parallel, validate the Langmuir isotherm assumptions discussed in section 3.2.

Development of a variable grid that could have a much finer mesh size near the reactor inlet (in the axial direction) and near the reactor wall (in the radial direction) is a potential improvement to the current work. One starting point to capture this behavior may be to implement a variable grid in one direction (either at the reactor inlet or at the channel wall), such as the one shown in Fig. 2.3. This approach to grid geometry assignment could also determine whether differences in transport coefficients near the inlet region or near the reactor wall have a bigger influence on predicted performance and correlation to experimental data. Figure 5.1 provides an example of a variable grid in two directions, with a finer grid both near the channel inlet and the channel walls.
Another possible piece of future work is focused around the matrix inversion mechanism. MATLAB, the program used to generate the transport correlation curves, selects its own inversion algorithm; however additional investigation could be made into the impacts of varying the inversion technique. Instability with the constant wall flux boundary condition may be able to be addressed by improving or modifying the solution technique. A marching (open-ended) solution scheme may improve the applicability of the constant wall-flux condition, at the potential expense of computational simplicity. As an intermediate step, an ADI scheme like the one described in section 5.1 may be appropriate.

The final recommendation for future work is to extend the scope of the experimental test program used to validate the model, as the boundary layer model was calibrated using data for a narrow range of flow conditions. Conducting a more extensive test program at a range of flow rates and external heat inputs is the most accurate method by which to calibrate the model. The kinetic catalyst effectiveness factor could be used as the calibration variable to correlate the model with the experimental data.
BIBLIOGRAPHY


### APPENDIX A – LENNARD-JONES PARAMETERS FOR DIFFUSIVITY

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Units: \(D_{AB} = \text{cm}^2/\text{s}\), \(\sigma_{AB} = \text{Å}\), \(T = \text{K}\) and \(p = \text{atm}\)

\[
D_{AB} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}}} \tag{A.1}
\]
APPENDIX B – SENSITIVITY STUDIES

B.1 Grid Size Sensitivity

The non-adiabatic, coupled chemical reaction-heat transfer model employs both kinetic and transport subroutines. As a result, the grid size can and should be optimized to minimize the numerical solution time while maintaining a mesh density that enables an accurate solution. The constant-property energy equation was studied for grid size sensitivity. Nusselt number with numbers of axial grid steps 40, 60, 80, 100, 140 and 200, along with numbers of radial grid steps 40, 60, 80, 100 and 140 was plotted against normalized axial length, z/dₙ in Figures B.1-5. For a given combination of axial and radial grid step numbers, MATLAB’s memory limited the grid size to that of the cases presented. The constant wall temperature condition was selected both for simplicity and for the availability of published analytical data (Incropera and Dewitt, 2002; Kays, Crawford and Weigand, 2005). The validation runs were performed for a tube 500 mm long, 5 mm in diameter, with 0.03504 g/s methane and steam mixture entering the tube at a S:C of 2.5 and constant properties at the inlet conditions. The channel geometry was selected to match the experimental GHSV, the initial temperature of the fuel mix was 415°C and the constant wall temperature was 675°C, to match the inlet design conditions imposed on the Modine reactor.
Figure B.1: Nusselt number vs. normalized axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and 40x30, 40, 60, 80, 100, 120 and 140 grid sizes.

Figure B.2: Nusselt number vs. normalized axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and 60x30, 40, 60, 80, 100 and 120 grid sizes.
Figure B.3: Nusselt number vs. normalized axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and 100x30, 40, 60 and 80 grid sizes.

Figure B.4: Nusselt number vs. normalized axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and 140x30, 40 and 60 grid sizes.
From Figures B.1-4, the asymptotic values do not change with number of axial steps. This useful result lead to the conclusion that axial grid size only determines the maximum Nusselt number at the inlet for the transport model, and has no bearing on the asymptotic value.

To determine whether further increases to the axial number of steps would yield a predicted inlet Nusselt number closer to the analytical value, 200x30 and 200x40 mesh sizes were run. The results are plotted in Figure B.5.

![Figure B.5: Nusselt number vs. normalized axial length for laminar flow in a circular tube with a constant wall temperature boundary condition for S:C=2.5 and 200x30 and 40 grid sizes.](image)

From the plots in this section and in Section 4.2.1, little difference can be seen between the 100x40 case and the 40x40 case; therefore, 40x40 is an appropriate grid size for the full-model.
B.2 Catalyst Effectiveness Factor Sensitivity

Following selection of a 40x40 grid, which focused on an increased-step number grid to improve transport accuracy, a sensitivity study around catalyst factor was conducted to ensure the kinetic model is predicting accurate methane conversion and molar flow rate. The study assumed a constant number of kinetic/species transport sub-iterations and number of full-model iterations (as shown in Figure 3.3). The 40x40 selected in Section 4.2.1 was used for this study. In Figure 4.7, a catalyst effectiveness factor of 12 had been shown to accurately predict methane conversion at each fuel mixture ratio. The catalyst factor impacts the species transport coefficients through the rate term applied at the wall boundary; a major assumption of this study is that the influence of catalyst factor to account for precious-metal reaction does not appreciably impact the species transport. Figure B.6 shows the methane Sherwood number curves for a S:C of 2.5 at three different catalyst factors: 4, 8 and 12 and a comparison to the curve for a catalyst factor of 1. From the plot, the above-described theory is confirmed (2% maximum average difference). H2 and CO2, the only constituents only present as product in the three mechanism reactions, are the most sensitive to catalyst factor; at catalyst factors of at least 4, a discontinuity exists in the Sherwood curve due to the excessive reaction rate of very low flow rates. However, the critical fully-developed value (used to model mass transport) exhibits a 7% maximum average difference over the last half of the tube. Figures B.6 and B.7 show the respective methane and steam Sherwood numbers and their [in]sensitivities to catalyst factor, justifying the section 4.4 assumption that the factor can be reduced to one when formulating transport coefficients.
Figure B.6: Methane Sherwood number sensitivity to catalyst effectiveness factor; 40x40 grid size, S:C=2.5.

Figure B.7: Steam Sherwood number sensitivity to catalyst effectiveness factor; 40x40 grid size, S:C=2.5.
APPENDIX C – SHERWOOD CORRELATION PLOTS

Figure C.1: Numerical steam Sherwood number vs. 2-part correlation for S:C=2.5 and 3.0.

Figure C.2: Numerical carbon monoxide Sherwood number vs. 2-part correlation for S:C=2.5 and 3.0.
Figure C.3: Numerical carbon dioxide Sherwood number vs. 2-part correlation for S:C=2.5 and 3.0.

Figure C.4: Numerical hydrogen Sherwood number vs. 2-part correlation for S:C=2.5 and 3.0.
APPENDIX D – CODE FOR TRANSPORT COEFFICIENT FORMULATION

% Adam S. Kimmel, B.S.Ch.E.
% HEAT AND MASS TRANSFER CORRELATIONS FOR STEAM METHANE REFORMING IN
% NON-ADIABATIC, PROCESS-INTENSIFIED CATALYTIC REACTORS
% Marquette University – Master's Thesis, August 2011
%
% tic;
% close all;
clear;
clic;

Nz=40; % number of axial steps
Nr=40; % number of radial steps

nz=Nz-1; % m
nr=Nr-1; % m
L=0.50; % m
dz=L/nz; % m (length of each box)
R=0.005; % m
dr=R/nr; % m (height of each box)
Aht=pi*(2*R)*L; % m^2
Aflow=pi*R^2; % m^2
As=2*pi*R; % m^2
V_rxtr=Aflow*L; % m^3

%S_C=2.5;
%S_C=3.0;

%steam to carbon ratio of inlet flow

% Properties (change pressure to bar)
Ru=8.314; % J/mol-K
PSMR=109375; % kg/m-s or Pa
P0=1.01325; % bar
Pt=1.09375; % bar
MWch4=16.04; % kg/kmol
MWh2o=18.02; % kg/kmol
MWco=28; % kg/kmol
MWco2=44; % kg/kmol
MWh2=2.02; % kg/kmol
MWn2=28; % kg/kmol

molwt(1)=MWch4;
molwt(2)=MWh2o;
molwt(3)=MWco;
molwt(4)=MWco2;
molwt(5)=MWh2;
molwt(6)=MWn2;
iteration=1;
maxit=5;

%-   -   -   -   -   -  -  -  -  -   -   -   -   -   -   -   -   -   -   -

INITIALIZE

for masterloop=1:300
    ENERGY
    for iter2=1:4
        KINETICS
        MASS_ch4
        MASS_h2o
        MASS_co
        MASS_co2
        MASS_h2
        MASS_n2
        PROPUPDATE
    end
    if masterloop>0
        xh2=molfrach2
    end
    if masterloop >0
        icck2011=masterloop
    end
    TRANSCOEFF
end

toc;

runtime=toc/60  % solve time in minutes
% SUBROUTINES
% INITIALIZE
% -- Energy initialization
massn2=0; % kg/s
if S_C==2.5
  mT=3.50406E-5; % kg/s;
end
if S_C==3
  mT=4.21607E-5; % kg/s;
end
% catalyst density from Froment and Bischoff, 1990
rho_bed=3.5; % kg_cat/m3
cat_factor=12;

% Property definitions
% Density (kg/m3)
rhoT(1:Nz,1:Nr)=0.30091;
% Heat capacity (J/kg-K)
cpT(1:Nz,1:Nr)=2654.7;
% Dynamic viscosity (N-s/m2 or kg/m-s)
muT(1:Nz,1:Nr)=2.8712E-5;
% Thermal conductivity (W/m-K or kg-m/s3-K)
kT(1:Nz,1:Nr)=0.09019;
% Reaction heat
qrxn(1:Nz) = 0;
% Initial Temp
T0=415+273;
Tcw=675+273;
Temp(1:Nz,1:Nr)=T0;
Temp(:,Nr)=Tcw;
% Specify wall temperature - this is assumed constant in
time, and based on
% simulation results by J. Valensa (MS Thesis, Marquette
University)
for i=1:Nz
  pos(i)=(i-1)*dz;
  axipos(i)=pos(i);
  if S_C==2.5
    Tw(i)=-187.43*(axipos(i))^2+228.91*(axipos(i))+876.54;
    if axipos(i)>0.5
      Tw(i)=Tw(i-1);
    end
  end
  if S_C==3
    Tw(i)=-251.43*(axipos(i))^2+276.91*(axipos(i))+868.74;
    if axipos(i)>0.5
      Tw(i)=Tw(i-1);
    end
  end
end
for i=1:Nz
  for j=1:Nr
    molfracch4(i,j)=1/(S_C+1)-0.0000015;
    molfrach2o(i,j)=S_C/(S_C+1)-0.0000015;
    molfracco(i,j)=0.000001;
    molfracco2(i,j)=0.000001;
    molfrach2(i,j)=0.000001;
    MWavg(i,j)=molfracch4(i,j)*MWch4+molfrach2o(i,j)*MWh2o+
    molfracco(i,j)*MWco+molfracco2(i,j)*MWco2+molfrach2(i,j)*MWh2;
    massch4(i,j)=molfracch4(i,j)*MWch4 /MWavg(i,j);
    massh2o(i,j)=molfrach2o(i,j)*MWh2o /MWavg(i,j);
    massco(i,j)=molfracco(i,j)*MWco /MWavg(i,j);
    massco2(i,j)=molfracco2(i,j)*MWco2 /MWavg(i,j);
    massh2(i,j)=molfrach2(i,j)*MWh2 /MWavg(i,j);
    summass=massch4(1,1)+massh2o(1,1)+massco(1,1)+
    massco2(1,1)+massh2(1,1);
    Con_ch4(i,j)=massch4(i,j)*mT;
    massh2o(i,j)=Con_h2o(i,j)*mT;
    massco(i,j)=Con_co(i,j)*mT;
    massco2(i,j)=Con_co2(i,j)*mT;
    massh2(i,j)=Con_h2(i,j)*mT;
    mT=massch4(1,1)+massh2o(1,1)+massco(1,1)+
    massco2(1,1)+massh2(1,1)+massn2(1,1);
    Con_ch4(i,j)=massch4(i,j)*mT;
    Con_h2o(i,j)=massh2o(i,j)*mT;
    Con_co(i,j)=massco(i,j)*mT;
    Con_co2(i,j)=massco2(i,j)*mT;
    Con_h2(i,j)=massh2(i,j)*mT;
    Con_n2(i,j)=massn2(i,j);
    rholc4(i,j)=Con_ch4(i,j)*rhoT(i,j);
    rholc2o(i,j)=Con_h2o(i,j)*rhoT(i,j);
    rholc(i,j)=Con_co(i,j)*rhoT(i,j);
    rholc2o(i,j)=Con_co2(i,j)*rhoT(i,j);
    rholc2(i,j)=Con_h2(i,j)*rhoT(i,j);
    rholn2(i,j)=Con_n2(i,j)*rhoT(i,j);
    molesch4(i,j)=Con_ch4(i,j)/MWch4;
    molesh2o(i,j)=Con_h2o(i,j)/MWh2o;
    molesco(i,j)=Con_co(i,j)/MWco;
    molesco2(i,j)=Con_co2(i,j)/MWco2;
    molesh2(i,j)=Con_h2(i,j)/MWh2;
    wch4_0=Con_ch4(1,1);
    wh2o_0=Con_h2o(1,1);
    wco_0=Con_co(1,1);
    wco2_0=Con_co2(1,1);
    wh2_0=Con_h2(1,1);
    wn2_0=Con_n2(1,1);
  end
end
% adjust mass average density and local velocity based on
% updated
density
for i=1:Nz
  vz_m(i)=mT/(rhoT(1,1)*Aflow);
  for j=1:Nr
    vz(i,j)=2*vz_m(i)*(1-((j-1)*dr/R)^2)+1e-10;
  end
end
wch4_0=Con_ch4(1,1);
wh2o_0=Con_h2o(1,1);
wco_0=Con_co(1,1);
wco2_0=Con_co2(1,1);
wh2_0=Con_h2(1,1);
wn2_0=Con_n2(1,1);
% PROUPDATE
% ENERGY
% for iter=1:maxit
%   iteration=iteration+1;
%   % Initialize coefficient matrix
%   Aa_T(1:(nz-1)*(nr-1),1:(nz-1)*(nr-1)) = 0;
%   % solve for only interior nodes and Neumann boundaries
%   % Transport equations
%   for i=1:nz
%     for j=nr:
%       khalf1=kTl(i,j);
%       khalf2=kTl(i,j);
%       for=<{j-2.5}/(j-2.5)}(j-1) khalf1/(dr^2);
%       for=<{j-0.5}/(j-0.5)}khalf2/(dr^2);
\( c = - \frac{(\rho T(i,j) \cdot c_p T(i,j) \cdot v_z(i,j))}{2 \cdot dz} \);
\( d = \frac{(\rho T(i,j) \cdot c_p T(i,j) \cdot v_z(i,j))}{2 \cdot dz} \);
\( e = 0 \);
\( f = \frac{((j - 0.5)/(j - 1) \cdot k_{half 2} + (j - 1.5)/(j - 1) \cdot k_{half 1})}{dr^2} \);

\begin{verbatim}
if masterloop > 20 % include property gradients in governing equation
    k_{half 1} = kT(i,j);
    k_{half 2} = kT(i,j);
    if j > 1
        k_{half 1} = 0.5*(kT(i,j) + kT(i,j-1));
        k_{half 2} = 0.5*(kT(i,j) + kT(i,j+1));
    end
    a = -(j-1.5)/(j-1)*k_{half 1}/(dr^2);
    b = -(j-0.5)/(j-1)*k_{half 2}/(dr^2);
    c = -(\rho T(i,j) \cdot c_p T(i,j) \cdot v_z(i,j)) / (2 \cdot dz);
    d = (\rho T(i,j) \cdot c_p T(i,j) \cdot v_z(i,j)) / (2 \cdot dz);
    if i > 2
        if i < Nz
            c = -(\rho T(i-1,j) \cdot c_p T(i-1,j) \cdot v_z(i-1,j)) / (2 \cdot dz);
            d = (\rho T(i+1,j) \cdot c_p T(i+1,j) \cdot v_z(i+1,j)) / (2 \cdot dz);
        end
        if i == 2
            % here utilize center node properties for inlet and outlet
            % coefficients
            c = -(\rho T(i-1,j) \cdot c_p T(i-1,j) \cdot v_z(i-1,j)) / (2 \cdot dz);
            d = (\rho T(i+1,j) \cdot c_p T(i+1,j) \cdot v_z(i+1,j)) / (2 \cdot dz);
        end
        if i == Nz
            % here both are reflected
            c = -(\rho T(i-1,j) \cdot c_p T(i-1,j) \cdot v_z(i-1,j)) / (2 \cdot dz);
            d = (\rho T(i+1,j) \cdot c_p T(i+1,j) \cdot v_z(i+1,j)) / (2 \cdot dz);
        end
    end
    e = 0;
    f = \frac{((j-0.5)/(j-1) \cdot k_{half 2} + (j-1.5)/(j-1) \cdot k_{half 1})}{dr^2};
end
end
% Boundary conditions
% no gradient along axis
if j == 2
    f = f + 4/3*a;
b = b - 1/3*a;
end
% no gradient at exit
if i == nz
    f = f + 4/3*d;
c = c - 1/3*d;
end
end
end
end
end

\( A = a/f; \)
\( B = b/f; \)
\( C = c/f; \)
\( D = d/f; \)
\( E = e/f; \)

% Formulation of the axial coefficient matrix \( A_T \)
% Energy
% middle of axial coefficient matrix
\( \text{number} = (i-2) \cdot (nr-1) \cdot (j-1); \)
% **** Change expression according to the reaction rate
\( Ba_T(\text{number}) = 0; \)
\( Ba_T(\text{number}, \text{number}) = A; \)
if j > 2
    \( Ba_T(\text{number, number-1}) = A; \)
end
if j < nr
    \( Ba_T(\text{number, number-1}) = B; \)
end
if i > 2
    \( Ba_T(\text{number, number- (nr-1)}) = C; \)
end
if i < nz
    \( Ba_T(\text{number, number+ (nr-1)}) = D; \)
end
% Boundary conditions
if j == nr
    Ba_T(number) = Ba_T(number) - \( B \cdot Tw(i); \)
    if masterloop == 1
        if iter == 1
            Ba_T(number) = Ba_T(number) - \( Ba_T(\text{number}) - C \cdot T0; \)
        else
            Ba_T(number) = Ba_T(number) - \( B \cdot Tw(i); \)
        end
    end
end
if i == 2
    Ba_T(number) = Ba_T(number) - \( C \cdot T0; \)
end
end
end

% apply BC's
for i = 1:Nz
    Temp(i, Nr) = Tw(i);
    % specified wall profile
    Temp(i, 1) = 4/3*Temp(i, 2) - 1/3*Temp(i, 3);
    % no gradient along axis
    end
    for j = 1:Nr
        Temp(nz, j) = 4/3*Temp(nz, 1) - 1/3*Temp(nz-1, j);
    end
    % force no gradient at exit, second-order backwards difference approximation of gradient
end
end
end

% PROPUPDATE

% KINETICS
% --------------------------------------------------------
% specify relaxation parameter to ensure stability of calculations.
% the compositional boundary values are dependent on the composition
% at the boundary, due to the reaction chemistry
\( relax = 1e-7; \)
if masterloop > 5
    relax = 1e-2;
end
if masterloop > 10
    relax = 2e-2;
end
if masterloop > 15
    relax = 3e-2;
end
if masterloop > 20
    relax = 4e-2;
end
if masterloop > 25
    relax = 6e-1;
end
if masterloop > 30
    relax = 8e-1;
end
if masterloop > 35
    relax = 1.0;
end
if masterloop > 40
    relax = 2e-1;
end
if masterloop > 45
    relax = 3e-1;
end
if masterloop > 50
    relax = 4e-1;
end
if masterloop > 55
    relax = 6e-1;
end
if masterloop > 60
    relax = 8e-1;
end

\( Ba_T(\text{number}) = Ba_T(\text{number}) - \)
\( B \cdot Tw(i); \)
if masterloop == 1
    if iter == 1
        Ba_T(number) = Ba_T(number) - \( Ba_T(\text{number}) - C \cdot T0; \)
    end
end
end
% end
for i=1:Nz

KeqSMR = 1.448e13 * exp(-221.9E3 / (Ru * Temp(i, Nr)));
KeqWGS = 2.151e-2 * exp(35.03E3 / (Ru * Temp(i, Nr)));
KeqRM = 3.116e11 * exp(-189.36E3 / (Ru * Temp(i, Nr)));
Kch4 = 6.65e-4 * exp(38.28E3 / (Ru * Temp(i, Nr)));
Kco = 8.23e-5 * exp(70.65E3 / (Ru * Temp(i, Nr)));
Kh2 = 6.12e-9 * exp(82.9E3 / (Ru * Temp(i, Nr)));
Kh2o = 1.77e5 * exp(-88.68E3 / (Ru * Temp(i, Nr)));
kSMR = 4.225e15 * exp(-240.1E3 / (Ru * Temp(i, Nr))) / 3600;

% kmol/s-kg_cat
kWGS = 1.955e6 * exp(-67.13E3 / (Ru * Temp(i, Nr))) / 3600;

% kmol/s-kg_cat
kRM = 1.020e15 * exp(-243.9E3 / (Ru * Temp(i, Nr))) / 3600;

% kPa
pch4 = rhoch4(i, Nr) / MWch4 * Ru * Temp(i, Nr) / 100;

% kPa
ph2o = rhoh2o(i, Nr) / MWh2o * Ru * Temp(i, Nr) / 100;

% kPa
pco = rhoco(i, Nr) / MWco * Ru * Temp(i, Nr) / 100;

% kPa
pco2 = rhoco2(i, Nr) / MWco2 * Ru * Temp(i, Nr) / 100;

% kPa
ph2 = rhoh2(i, Nr) / MWh2 * Ru * Temp(i, Nr) / 100;

DEN = 1 + Kco * pco + Kh2 * ph2 + Kch4 * pch4 + Kh2o * ph2o / ph2;

rSMR = kSMR / ph2^2.5 * (pch4 * ph2o - ph2^3 * pco / KeqSMR) / DEN^2;
rWGS = kWGS / ph2 * (pco * ph2o - ph2 * pco2 / KeqWGS) / DEN^2;
rRM = kRM / ph2^3.5 * (pch4 * ph2o^2 - ph2^4 * pco2 / KeqRM) / DEN^2;

rSMR = rSMR * cat_factor;
rWGS = rWGS * cat_factor;
rRM = rRM * cat_factor;

rch4(i) = - (rSMR + rRM) * MWch4;

rh2o(i) = (- rSMR - 2 * rRM - rWGS) * MWh2o;
rco2(i) = (rWGS + rRM) * MWco2;
rco(i) = (rSMR + rRM) * MWco;

rh2(i) = (3 * rSMR + 4 * rRM + rWGS) * MWh2;

rn2(i) = 0;

% specify compositions based on reaction rates and diffusion from cell

wch4_bc(i) = (rhoT(i, Nr) / rhoT(i, Nz)) * Con_ch4(i, Nr) +
            dr / Dch4(i, j) * rch4(i) *
            rho_bed / rhoT(i, Nz) * R / 2 * relax;

if wch4_bc(i) < 0
    wch4_bc(i) = 0;
end

wh2o_bc(i) = (rhoT(i, Nr) / rhoT(i, Nz)) * Con_h2o(i, Nr) +
            dr / Dh2o(i, j) * rh2o(i) *
            rho_bed / rhoT(i, Nz) * R / 2 * relax;

if wh2o_bc(i) < 0
    wh2o_bc(i) = 1e-6;
end

wco2_bc(i) = (rhoT(i, Nr) / rhoT(i, Nz)) * Con_co2(i, Nr) +
            dr / Dco2(i, j) * rco2(i) *
            rho_bed / rhoT(i, Nz) * R / 2 * relax;

if wco2_bc(i) < 0
    wco2_bc(i) = 1e-6;
end

wco_bc(i) = (rhoT(i, Nr) / rhoT(i, Nz)) * Con_co(i, Nr) +
            dr / Dco(i, j) * rco(i) *
            rho_bed / rhoT(i, Nz) * R / 2 * relax;

if wco_bc(i) < 0
    wco_bc(i) = 1e-6;
end

wn2_bc(i) = (rhoT(i, Nr) / rhoT(i, Nz)) * Con_n2(i, Nr) +
            dr / Dn2(i, j) * rn2(i) *
            rho_bed / rhoT(i, Nz) * R / 2 * relax;

if wn2_bc(i) < 0
    wn2_bc(i) = 1e-6;
end

% ensure mass fractions sum to 1.0

sum = wch4_bc(i) + wh2o_bc(i) + wco_bc(i) + wco2_bc(i) + wh2_bc(i) + wn2_bc(i);

wch4_bc(i) = wch4_bc(i) / sum;
wh2o_bc(i) = wh2o_bc(i) / sum;
wco_bc(i) = wco_bc(i) / sum;
wco2_bc(i) = wco2_bc(i) / sum;
wh2_bc(i) = wh2_bc(i) / sum;
wn2_bc(i) = wn2_bc(i) / sum;

end

% MASS CH4
%--------------------------------------------------------
% Initialize coefficient matrix

Aa_wch4(1:(nz-1) * (nr-1), 1:(nz-1) * (nr-1)) = 0;

% solve for only interior nodes and Neumann boundaries
for j = 2:nr
    for i = 2:nz
        Dch4half1 = Dch4(i, j) * rhoT(i, j);
        Dch4half2 = Dch4(i, j) * rhoT(i, j);

        a = -(j-1.5) / (j-1) * Dch4half1 / (dr^2);
        b = -(j-0.5) / (j-1) * Dch4half2 / (dr^2);

        if masterloop > 20
            % include property gradients in governing equation
            Dch4half1 = Dch4(i, j) * rhoT(i, j);
            Dch4half2 = Dch4(i, j) * rhoT(i, j);
        end

        if j > 1
            Dch4half1 = 0.5 * (Dch4(i, j) + Dch4(i, j-1)) * rhoT(i, j-1);
            Dch4half2 = 0.5 * (Dch4(i, j) + Dch4(i, j+1)) * rhoT(i, j+1);
        end

        % Boundary conditions
        %..no gradient along axis
        if j == 2
            a = -1/3 * a;
        end

        %..no gradient at exit
        if i == nz
            b = -1/3 * b;
        end

        a = a / f;
        b = b / f;
        c = c / f;
        d = d / f;
        e = e / f;

        % Formulation of the axial coefficient matrix A_T
        % middle of axial coefficient matrix (tridiagonal terms)
        number = (i-2) * (nr-1) + (j-1);

        Aa_wch4(number, number) = a;
        Aa_wch4(number, number-1) = b;
        Aa_wch4(number, number+1) = c;
        Aa_wch4(number, number+2) = d;
        Aa_wch4(number, number+3) = e;
% ***** Change expression according to the reaction rate
Ba_wch4(number) = 0;
Aa_wch4(number,number) = 1;
if j>2
    Aa_wch4(number,number-1) = A;
end
if j<nr
    Aa_wch4(number,number+1) = B;
end
if i>2
    Aa_wch4(number,number-(nr-1)) = C;
end
if i<nz
    Aa_wch4(number,number+(nr-1)) = D;
end
% Boundary conditions
if j==nr
    Ba_wch4(number) = Ba_wch4(number) - B*wch4_bc(i);
end
if i==2
    Ba_wch4(number) = Ba_wch4(number) - C*wch4_0;
end
end
end
wch4 = Aa_wch4 \\ Ba_wch4';
%           solve for only interior nodes and Neumann boundaries
for i=2:nz
    for j=2:nr
        number = (i-2)*(nr-1)+(j-1);
        Con_ch4(i,j) = wch4(number);
    end
end
%apply BC's
for i=1:Nz
    Con_ch4(i,Nr) = wh2o_bc(i);
    Con_ch4(i,1) = 4/3*Con_ch4(i,2) - 1/3*Con_ch4(i,3);
end
for j=1:Nr
    Con_h2o(j,Nz) = wh2o_0;
end
% MASS H2O
%--------------------------------------------------------
% Initialize coefficient matrix
Aa_wh2o(1:(nz-1)*(nr-1),1:(nz-1)*(nr-1)) = 0;
% solve for only interior nodes and Neumann boundaries
for i=2:nz
    for j=2:nr
        number = (i-2)*(nr-1)+(j-1);
        Con_ch4(i,j) = wch4(number);
    end
end
%apply BC's
for i=1:Nz
    Con_ch4(i,Nr) = wh2o_bc(i);
    Con_ch4(i,1) = 4/3*Con_ch4(i,2) - 1/3*Con_ch4(i,3);
end
for j=1:Nr
    Con_h2o(j,Nz) = wh2o_0;
end
% Formulation of the axial coefficient matrix A_T
% middle of axial coefficient matrix (tridiagonal terms)
number = (i-2)*(nr-1)+(j-1);
% ***** Change expression according to the reaction rate
Ba_wh2o(number) = 0;
Aa_wh2o(number,number) = 1;
if j>2
    Aa_wh2o(number,number-1) = A;
end
if j<nr
    Aa_wh2o(number,number+1) = B;
end
if i>2
    Aa_wh2o(number,number-(nr-1)) = C;
end
if i<nz
    Aa_wh2o(number,number+(nr-1)) = D;
end
% Boundary conditions
if j==nr
    Ba_wh2o(number) = Ba_wh2o(number) - B*wh2o_bc(i);
end
if i==2
    Ba_wh2o(number) = Ba_wh2o(number) - C*wh2o_0;
end
end
end
wh2o = Aa_wh2o \\ Ba_wh2o';
for j=1:Nr
conch2o=Con_h2o(nz,j);
Con_h2o(1,j)=wh2o_0;
%inlet conc
Con_h2o(Nz,j)=4/3*Con_h2o(nz,j)-1/3*Con_h2o(nz-1,j);
%force no gradient at exit, second-order backwards difference approximation of gradient
end
for i=1:Nz
for j=1:Nr
if Con_h2o(i,j)<0
Con_h2o(i,j)=1e-8;
end
molfrach2o(i,j)=Con_h2o(i,j)/MWh2o*MWavg(i,j);
end
end
% MASS CO
%--------------------------------------------------------
% Initialize coefficient matrix
Aa_wco(1:(nz-1)*(nr-1),1:(nz-1)*(nr-1)) = 0;
% solve for only interior nodes and Neumann boundaries
for i=2:nz
for j=2:nr
Dcohalf1=Dco(i,j) *rhoT(i,j);
Dcohalf2=Dco(i,j) *rhoT(i,j);
a=-(j-1.5)/(j-1)*Dcohalf1/(dr^2);
b=-(j-0.5)/(j-1)*Dcohalf2/(dr^2);
c=-(rhoT(i,j)*vz(i,j))/(2*dz);
d=(rhoT(i,j)*vz(i,j))/(2*dz);
e=0;
f=((j-0.5)/(j-1)*Dcohalf2+(j-1.5)/(j-1)*Dcohalf1)/(dr^2);
end
end
% Boundary conditions
if j==nr
Ba_wco(number)=Ba_wco(number)-B*wco_bc(i);
end
if i==2
Ba_wco(number)=Ba_wco(number)-C*wco_0;
end
end
wco=Aa_wco\Ba_wco';
% solve for only interior nodes and Neumann boundaries
for i=2:nz
for j=2:nr
number = (i-2)*(nr-1)+(j-1);
Con_co(i,j) = wco(number);
end
end
% apply BC's
for i=1:Nz
Con_co(i,Nr)=wco_bc(i);
Con_co(i,1)=4/3*Con_co(i,2)-1/3*Con_co(i,3);
end
for j=1:Nr
end
concco=Con_co(nz,j);
Con_co(1,j)=wco_0;
Con_co(Nz,j)=4/3*Con_co(nz,j)-1/3*Con_co(nz-1,j);
%force no gradient at exit, second-order backwards difference approximation of gradient
end
for i=1:Nz
for j=1:Nr
if Con_co(i,j)<0
Con_co(i,j)=1e-8;
end
molfracco(i,j)=Con_co(i,j)/MWco*MWavg(i,j);
end
end
% MASS CO2
%--------------------------------------------------------
% Initialize coefficient matrix
Aa_wco2(1:(nz-1)*(nr-1),1:(nz-1)*(nr-1)) = 0;
% solve for only interior nodes and Neumann boundaries
for i=2:nz
for j=2:nr
Dco2half1=Dco2(i,j) *rhoT(i,j);
Dco2half2=Dco2(i,j) *rhoT(i,j);
a=-(j-1.5)/(j-1)*Dco2half1/(dr^2);
b=-(j-0.5)/(j-1)*Dco2half2/(dr^2);
c=-(rhoT(i,j)*vz(i,j))/(2*dz);
d=(rhoT(i,j)*vz(i,j))/(2*dz);
e=0;
f=((j-0.5)/(j-1)*Dco2half2+(j-1.5)/(j-1)*Dco2half1)/(dr^2);
end
end
% Boundary conditions
%...no gradient along axis
if j==nr
Ba_wco2(number)=Ba_wco2(number)-B*wco_bc(i);
end
if i==2
Ba_wco2(number)=Ba_wco2(number)-C*wco_0;
end
end
wco=Aa_wco2\Ba_wco2';
% solve for only interior nodes and Neumann boundaries
for i=2:nz
for j=2:nr
number = (i-2)*(nr-1)+(j-1);
Con_co2(i,j) = wco2(number);
end
end
% apply BC's
for i=1:Nz
Con_co2(i,Nr)=wco_bc(i);
Con_co2(i,1)=4/3*Con_co2(i,2)-1/3*Con_co2(i,3);
end
%...no gradient at exit, second-order backwards difference approximation of gradient
end
for i=1:Nz
for j=1:Nr
if Con_co2(i,j)<0
Con_co2(i,j)=1e-8;
end
molfracco(i,j)=Con_co2(i,j)/MWco*MWavg(i,j);
end
end
% MASS CO2
%--------------------------------------------------------
if j>1
  Dco2half1 = 0.5*(Dco2(i,j)+Dco2(i,j-1))
  Dco2half2 = 0.5*(Dco2(i,j)+Dco2(i,j+1))
end

for i=1:Nz
  c=-((j-0.5)/(j-1)*Dco2half2)/(dr^2);
  d=((j-0.5)/(j-1)*Dco2half1)/(dr^2);
e=0;
  ((j-0.5)/(j-1)*Dco2half2+(j-1.5)/(j-1)*Dco2half1)/(dr^2);
end

% Boundary conditions
% no gradient along axis
if j==2
  b=-1/3*a;
end
% no gradient at exit
if i==Nz
  c=-1/3*d;
end
if i==2
  c=-(rhoT(i,j)*vz(i,j))/(2*dz);
  d=(rhoT(i,j)*vz(i,j))/(2*dz);
end

for i=1:Nz
  Con_co2(i,j) = wco2*(number);
  Con_co2(i,Nr)=wco2_bc(i);
  Con_co2(i,1)=4/3*Con_co2(i,2)-1/3*Con_co2(i,3);
end

end

% MASS H2
%--------------------------------------------------------
% Initialize coefficient matrix Aa_wco2

% Formulation of the axial coefficient matrix A_T terms
% middle of axial coefficient matrix (tridiagonal terms)
% **** *** Change expression according to the reaction rate
number = (i-2)*(nr-1)+(j-1);
\[
A = a/f; \\
B = b/f; \\
C = c/f; \\
D = d/f; \\
E = e/f;
\]

% Formulation of the axial coefficient matrix \( A_T \)
% middle of axial coefficient matrix (tridiagonal terms)

number = (i-2)*(nr-1)+(j-1);

% ***** Change expression according to the reaction rate

\[
Ba_\text{wh2}(number) = 0;
Aa_\text{wh2}(number,number)=1;
\]

if \( j>2 \)
\[
Aa_\text{wh2}(number,number-1)=A;
\]
end

if \( j<nr \)
\[
Aa_\text{wh2}(number,number+1)=B;
\]
end

if \( i>2 \)
\[
Aa_\text{wh2}(number,number-(nr-1))=C;
\]
end

if \( i<nz \)
\[
Aa_\text{wh2}(number,number+(nr-1))=D;
\]
end

% Boundary conditions

if \( j==nr \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-B*\text{wh2}_{bc}(i);
\]
end

if \( i==2 \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-C*\text{wh2}_0;
\]
end

end

end

\[
\text{wh2}=Aa_\text{wh2}\backslash Ba_\text{wh2}';
\]

% solve for only interior nodes and Neumann boundaries

for \( i=2:nz \)
for \( j=2:nr \)
\[
\text{Dn2half1} = \text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
\[
\text{Dn2half2} = \text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
\[
a=-(j-1.5)/(j-1) * \text{Dn2half1}/(dr^2);
\]
\[
b=-(j-0.5)/(j-1) * \text{Dn2half2}/(dr^2);
\]
\[
c=(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
d=(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
e=0;
\]
\[
f=((j-0.5)/(j-1) * \text{Dn2half2} + (j-1.5)/(j-1) * \text{Dn2half1})/(dr^2);
\]
end
end

if masterloop>20
% include property gradients in governing equation

\[
\text{Dn2half1}=\text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
\[
\text{Dn2half2}=\text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
end

\[
\text{a}=-((j-1.5)/(j-1)) * \text{Dn2half1}/(dr^2);
\]
\[
\text{b}=-((j-0.5)/(j-1)) * \text{Dn2half2}/(dr^2);
\]
\[
\text{c}=(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
\text{d}=(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
e=0;
\]
\[
f=((j-0.5)/(j-1) * \text{Dn2half2} + (j-1.5)/(j-1) * \text{Dn2half1})/(dr^2);
\]
end

\[
\text{Ba_\text{wh2}(number) = 0;}
Aa_\text{wh2}(number,number)=1;
\]

if \( j>2 \)
\[
Aa_\text{wh2}(number,number-1)=A;
\]
end

if \( j<nr \)
\[
Aa_\text{wh2}(number,number+1)=B;
\]
end

if \( i>2 \)
\[
Aa_\text{wh2}(number,number-(nr-1))=C;
\]
end

if \( i<nz \)
\[
Aa_\text{wh2}(number,number+(nr-1))=D;
\]
end

% Boundary conditions

if \( j==nr \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-B*\text{wh2}_{bc}(i);
\]
end

if \( i==2 \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-C*\text{wh2}_0;
\]
end

end

end

\[
\text{wh2}=Aa_\text{wh2}\backslash Ba_\text{wh2}';
\]

% solve for only interior nodes and Neumann boundaries

for \( i=2:nz \)
for \( j=2:nr \)
\[
\text{Dn2half1} = \text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
\[
\text{Dn2half2} = \text{Dn2}(i,j) * \text{rhoT}(i,j);
\]
\[
a=-(j-1.5)/(j-1) * \text{Dn2half1}/(dr^2);
\]
\[
b=-(j-0.5)/(j-1) * \text{Dn2half2}/(dr^2);
\]
\[
c=-(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
d=(\text{rhoT}(i,j) * \text{vz}(i,j))/((2*dz));
\]
\[
e=0;
\]
\[
f=((j-0.5)/(j-1) * \text{Dn2half2} + (j-1.5)/(j-1) * \text{Dn2half1})/(dr^2);
\]
end
end

%Boundary conditions

\[
\text{Ba_\text{wh2}(number) = 0;}
Aa_\text{wh2}(number,number)=1;
\]

if \( j>2 \)
\[
Aa_\text{wh2}(number,number-1)=A;
\]
end

if \( j<nr \)
\[
Aa_\text{wh2}(number,number+1)=B;
\]
end

if \( i>2 \)
\[
Aa_\text{wh2}(number,number-(nr-1))=C;
\]
end

if \( i<nz \)
\[
Aa_\text{wh2}(number,number+(nr-1))=D;
\]
end

% Boundary conditions

if \( j==nr \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-B*\text{wh2}_{bc}(i);
\]
end

if \( i==2 \)
\[
Ba_\text{wh2}(number)=Ba_\text{wh2}(number)-C*\text{wh2}_0;
\]
end

end

end

\[
\text{wh2}=Aa_\text{wh2}\backslash Ba_\text{wh2}';
\]
% solve for only interior nodes and Neumann boundaries
for i=2:nz
    for j=2:nr
        number = (i-2)*(nr-1)+(j-1);
        Con_n2(i,j) = wn2(number);
    end
end
apply BC's
for i=1:Nz
    Con_n2(i,Nr)=wn2_bc(i);
end
%wall concentration
Con_n2(i,1)=4/3*Con_n2(i,2)-1/3*Con_n2(i,3);
%no gradient along axis
for j=1:Nr
    endconcn2=Con_n2(nz,j);
end
%inlet conc
Con_n2(Nz,j)=4/3*Con_n2(nz,j)-1/3*Con_n2(nz-1,j);
%force no gradient at exit, second-order backwards difference approximation of gradient
for i=1:Nz
    for j=1:Nr
        if Con_n2(i,j)<0
            Con_n2(i,j)=1e-8;
        end
        molfracn2(i,j)=Con_n2(i,j)/MWn2*MWavg(i,j);
    end
end
%PROPUPDATE
%--------------------------------------------------------
% Property, velocity, and bulk fluid density update
% (to be run after transport loop module)
for i=1:Nz
    for j=1:Nr
        if iteration>1
            %normalizing node mole/mass fractions
            for kkk=1:3
                MWavg(i,j)=molfracch4(i,j)*MWch4+molfrach2o(i,j)*MWh2o+molfracco(i,j)*MWco+
                            molfracco2(i,j)*MWco2+molfrach2(i,j)*MWh2;
            end
            massch4(i,j)=molfracch4(i,j)*MWch4/MWavg(i,j);
            massh2o(i,j)=molfrach2o(i,j)*MWh2o/MWavg(i,j);
            massco(i,j)=molfracco(i,j)*MWco/MWavg(i,j);
            massco2(i,j)=molfracco2(i,j)*MWco2/MWavg(i,j);
            massh2(i,j)=molfrach2(i,j)*MWh2/MWavg(i,j);
            summass=massch4(i,j)+massh2o(i,j)+massco(i,j)+
                        massco2(i,j)+massh2(i,j)+ massn2(i,j);
            Con_ch4(i,j)=massch4(i,j)/summass;
            Con_h2o(i,j)=massh2o(i,j)/summass;
            Con_co(i,j)=massco(i,j)/summass;
            Con_co2(i,j)=massco2(i,j)/summass;
            Con_h2(i,j)=massh2(i,j)/summass;
            Con_n2(i,j)=massn2(i,j)/summass;
            molfracch4(i,j)=Con_ch4(i,j)/MWch4*MWavg(i,j);
            molfrach2o(i,j)=Con_h2o(i,j)/MWh2o*MWavg(i,j);
            molfracco(i,j)=Con_co(i,j)/MWco*MWavg(i,j);
            molfracco2(i,j)=Con_co2(i,j)/MWco2*MWavg(i,j);
            molfrach2(i,j)=Con_h2(i,j)/MWh2*MWavg(i,j);
            molfracn2(i,j)=Con_n2(i,j)/MWn2;
        end
        % Density (kg/m3)
        rhoch4(i,j)=PSMR*molfracch4(i,j)*MWch4/(Ru*Temp(i,j));
        rhoh2o(i,j)=PSMR*molfrach2o(i,j)*MWh2o/(Ru*Temp(i,j));
        rhoco(i,j)=PSMR*molfracco(i,j)*MWco/(Ru*Temp(i,j));
        rhoco2(i,j)=PSMR*molfracco2(i,j)*MWco2/(Ru*Temp(i,j));
        rhoh2(i,j)=PSMR*molfrach2(i,j)*MWh2/(Ru*Temp(i,j));
        rhon2(i,j)=PSMR*molfran2(i,j)*MWn2/(Ru*Temp(i,j));
        rhoT(i,j)=rhoT(i,j)+rhoch4(i,j)+rholh2o(i,j)+rholco(i,j)+rholco2(i,j)+
                   rhoh2(i,j)+ rho2n(i,j);
        % Heat capacity (J/kg-K)
cpch4(i,j)=(33295+80295*((2102/Temp(i,j))/(sinh(2102/Temp(i,j))))^2+
                          42130*((995/Temp(i,j))/(cosh(995/Temp(i,j))))^2)/MWch4;
cph2o(i,j)=(33359+26798*((2609/Temp(i,j))/(sinh(2609/Temp(i,j))))^2+
                        3760*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWh2;
cpco(i,j)=(29108+8773*((3085/Temp(i,j))/(sinh(3085/Temp(i,j))))^2+
                               8455*((1538/Temp(i,j))/(cosh(1538/Temp(i,j))))^2)/MWco;
cpco2(i,j)=(29370+34540*(((-1428)/Temp(i,j))/(sinh((-1428)/Temp(i,j))))^2+
                                      26400*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWco2;
cph2(i,j)=(27617+9560*((2466/Temp(i,j))/(sinh(2466/Temp(i,j))))^2+
                                   3760*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWh2;
cpco2(i,j)=(29108+8773*((3085/Temp(i,j))/(sinh(3085/Temp(i,j))))^2+
                               8455*((1538/Temp(i,j))/(cosh(1538/Temp(i,j))))^2)/MWco;
cpco2(i,j)=(29370+34540*(((-1428)/Temp(i,j))/(sinh((-1428)/Temp(i,j))))^2+
                                      26400*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWco2;
cpco2(i,j)=(29370+34540*(((-1428)/Temp(i,j))/(sinh((-1428)/Temp(i,j))))^2+
                                      26400*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWco2;
cpco2(i,j)=(29370+34540*(((-1428)/Temp(i,j))/(sinh((-1428)/Temp(i,j))))^2+
                                      26400*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWco2;
cpco2(i,j)=(29370+34540*(((-1428)/Temp(i,j))/(sinh((-1428)/Temp(i,j))))^2+
                                      26400*((588/Temp(i,j))/(cosh(588/Temp(i,j))))^2)/MWco2;
pT(i,j)=rhoch4(i,j)+rhoh2o(i,j)+rhoco(i,j)+rhoco2(i,j)+
                   rhoh2(i,j)+ rho2n(i,j);
        % Dynamic viscosity (N-s/m2 or kg/m-s)
much4(i,j)=(0.00001323*(Temp(i,j))^-0.1798)/(1+718/Temp(i,j)-8900/
                              (Temp(i,j))^2);
muh2o(i,j)=(0.000002699*(Temp(i,j))^-0.498)/(1+1258/Temp(i,j)-19570/
                              (Temp(i,j))^2);
muco(i,j)=(0.000001113*(Temp(i,j))^-0.5383)/(1+94.7/Temp(i,j)+0/
                              (Temp(i,j))^2);
muco2(i,j)=(0.000002148*(Temp(i,j))^-0.46)/(1+290/Temp(i,j)+0/
                              (Temp(i,j))^2);
muh2(i,j)=(0.000000156*(Temp(i,j))^-0.706)/(1-5.87/Temp(i,j)+210/
                              (Temp(i,j))^2);
mun2(i,j)=(0.000000763*(Temp(i,j))^-0.588)/(1-67.8/Temp(i,j)+0/
                              (Temp(i,j))^2);
        eta(1)=much4(i,j);
        eta(2)=muh2o(i,j);
        eta(3)=muco(i,j);
        eta(4)=muco2(i,j);
        eta(5)=muh2(i,j);
        eta(6)=mun2(i,j);
        % Thermal conductivity (W/m-K or kg-m/s3-K)
        kch4(i,j)=(0.001266*(Temp(i,j))^-0.8031)/(1+960/Temp(i,j)-61200/
                              (Temp(i,j))^2);
kho2(i,j)=(0.00006977*(Temp(i,j))^-1.243)/(1+844.9/Temp(i,j)-148850/
                              (Temp(i,j))^2);
        kco(i,j)=(0.000839*(Temp(i,j))^-0.592)/(1+86.05/Temp(i,j)+0/
                              (Temp(i,j))^2);
\[ k_{co2}(i,j) = (3.69 \times (Temp(i,j))^{-0.3838}) / (1 + 964/Temp(i,j) + 186000/(Temp(i,j))^2); \]
\[ k_{h2}(i,j) = (0.002547 \times (Temp(i,j))^{0.7444}) / (1 + 9/Temp(i,j) + 0/(Temp(i,j))^2); \]
\[ k_{n2}(i,j) = (0.000351 \times (Temp(i,j))^{0.7652}) / (1 + 26/Temp(i,j) + 0/(Temp(i,j))^2); \]
\[ k_{th}(1) = k_{ch4}(i,j); \]
\[ k_{th}(2) = k_{h2o}(i,j); \]
\[ k_{th}(3) = k_{co}(i,j); \]
\[ k_{th}(4) = k_{co2}(i,j); \]
\[ k_{th}(5) = k_{h2}(i,j); \]
\[ for \ k1=1:6 \]
\[ faij(k1,k1) = 1.0; \]
\[ gaij(k1,k1) = 1.0; \]
\[ if \ k1<5 \]
\[ nk=k1+1; \]
\[ for \ k2=nk:6 \]
\[ faij(k1,k2) = (1.0 + (eta(k1)/eta(k2))^{0.5} \times (molwt(k2)/molwt(k1))^{0.25})^2.0 / (8.0^{0.5} \times (1.0 + molwt(k1)/molwt(k2))^{0.5}); \]
\[ for \ k2=1:6 \]
\[ sum2=sum2+faij(k1,k2) \times x(k2); \]
\[ end \]
\[ for \ k1=1:6 \]
\[ sum1=sum1+x(k1) \times eta(k1)/sum2; \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ x(1)=molfracch4(i,j); \]
\[ x(2)=molfrach2o(i,j); \]
\[ x(3)=molfracco(i,j); \]
\[ x(4)=molfracco2(i,j); \]
\[ x(5)=molfrach2(i,j); \]
\[ x(6)=molfracn2(i,j); \]
\[ sum1=0; \]
\[ sum3=0; \]
\[ for \ k1=1:6 \]
\[ sum2=0; \]
\[ sum4=0; \]
\[ for \ k2=1:6 \]
\[ sum2=sum2+faij(k1,k2) \times x(k2); \]
\[ end \]
\[ sum1=sum1+x(k1) \times eta(k1)/sum2; \]
\[ sum3=sum3+x(k1) \times k_{th}(k1)/sum2; \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ end \]
\[ \% Diffusivity coefficient mixing rule (m^2/s) \]
\[ for \ i=1:Nz \]
\[ end \]
\[ end \]
\[ \% MIXCUP_PROPUPDATE \]
\[ \% Mixing-cup property update \]
\[ \% determines axially-dependent bulk properties to be used \]
\[ \% in the transport coefficient calculations \]
\[ for \ i=1:Nz \]
\[ end \]

```
% Diffusivity coefficient mixing rule (m^2/s)
for i=1:Nz
    for j=1:Nr
        Dch4h2o(i,j) = 0.0000000001 \times (Temp(i,j))^{2+0.00000009 \times (Temp(i,j))-0.000062};
        Dch4co(i,j) = 0.0000000009 \times (Temp(i,j))^{2+0.00000009 \times (Temp(i,j))-0.000062};
        Dch4co2(i,j) = 0.00000000007 \times (Temp(i,j))^{2+0.00000009 \times (Temp(i,j))-0.000055};
        Dch4h2(i,j) = 0.000000000003 \times (Temp(i,j))^{2+0.000000001 \times (Temp(i,j))-0.000002};
        Dch4co2(i,j) = 0.0000000000009 \times (Temp(i,j))^{2+0.00000000001 \times (Temp(i,j))-0.000001};
        Dch4h2(i,j) = 0.000000000000003 \times (Temp(i,j))^{2+0.000000000001 \times (Temp(i,j))-0.0000005};
    end
end
```
\[ dmTtemp(i) = dmTtemp(i) + \rho_T(i,j) \cdot c_p_T(i,j) \cdot vz(i,j) \cdot Dbn2(i) = Dbn2(i) + Dn2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ Dbh2(i) = Dbh2(i) + Dh2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ Dbco(i) = Dbco(i) + Dco(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ Dbh2o(i) = Dbh2o(i) + Dh2o(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ Dbch4(i) = Dbch4(i) + Dch4(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ 1)*dr)*dr); \]
\[ rhobT(i) = rhobT(i) + \mu_T(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ kbT(i) = kbT(i) + kT(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ cpbT(i) = cpbT(i) + \rho_T(i,j) \cdot vz(i,j) \cdot dr; \]
\[ checker = checker + ((j-1) \cdot dr) \cdot dr; \]
\[ yn2(i) = yn2(i) + 0.5 \cdot \rho_n2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ yco2(i) = yco2(i) + 0.5 \cdot \rho_co2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ yh2o(i) = yh2o(i) + 0.5 \cdot \rho_h2o(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ ych4(i) = ych4(i) + 0.5 \cdot \rho_ch4(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ Temp(i,j) = Temp(i,j) + Temp(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ yco(i) = yco(i) + 0.5 \cdot \rho_co(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ yh2(i) = yh2(i) + 0.5 \cdot \rho_h2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ yn2(i) = yn2(i) + 0.5 \cdot \rho_n2(i,j) \cdot ((j-1) \cdot dr) \cdot dr; \]
\[ vz(i,Nr)/vz_m(i) * (1-0.5*dr/R)^2; \]
\[ mT(i,Nr) = mT * rhoT(i,Nr)/rhobT(i) * vz(i,1)/vz_m(i) \]
\[ yco2(i) = yco2(i) * 2*pi/Aflow; \]
\[ ych4(i) = ych4(i) * 2*pi/Aflow; \]
\[ Dbco2(i) = Dbco2(i) * 2*pi/Aflow; \]
\[ mch4(i,j)=Con_ch4(i,j)*dmT(i,j); \]
\[ mh2(i,j)=Con_h2(i,j)*dmT(i,j); \]
\[ mn2(i,j)=Con_n2(i,j)*dmT(i,j); \]
\[ mco(i,j)=Con_co(i,j)*dmT(i,j); \]
\[ mco2(i,j)=Con_co2(i,j)*dmT(i,j); \]
\[ massn2(i,j)=molfracn2(i,j)*MWn2 /MWavg(i,j); \]
\[ massco(i,j)=molfracco(i,j)*MWco /MWavg(i,j); \]
\[ massh2o(i,j)=molfrach2o(i,j)*MWh2o /MWavg(i,j); \]
\[ summoles(i,j)=mollesch4(i,j)+mollesh2(i,j)+mollesco(i,j)+mollesn2(i,j); \]
\[ molfrach2o(i,j)=molfrach2o(i,j)/summoles(i,j); \]
\[ molfracch4(i,j)=molfracch4(i,j)/summoles(i,j); \]
\[ MWh2o(i,j)=molfrach2o(i,j)*MWh2o/molesh2o(i,j); \]
\[ MWco(i,j)=molfracco(i,j)*MWco/molesco(i,j); \]
\[ MWn2(i,j)=molfrancn2(i,j)*MWn2/molesn2(i,j); \]
\[ MWavg(i,j)=molfracch4(i,j)*MWch4+molfrach2(i,j)*MWh2+molfracn2(i,j)*MWn2+molfraco2(i,j)*MWco2+molfraco(i,j)*MWco; \]
\[ density(i)=rho(i)/MWavg(i,j); \]
summass=massch4(i,j)+massh2o(i,j)+massco(i,j)+massco2(i,j)+massh2(i,j)+massn2(i,j);
Con_ch4(i,j)=massch4(i,j)/summass;
Con_h2o(i,j)=massh2o(i,j)/summass;
Con_co(i,j)=massco(i,j)/summass;
Con_co2(i,j)=massco2(i,j)/summass;
Con_h2(i,j)=massh2(i,j)/summass;
Con_n2(i,j)=massn2(i,j)/summass;
end
end

%TRANSCOEF

% Transport coefficients
% compute Nusselt and Sherwood numbers for flow in the pipe
for i=2:Nz
    z(i)=(i-1)/nz*L;
    h(i)=kbT(i)*((Tw(i)-Temp(i,nr))/dr)./((Tw(i) -(Tb(i))));
    hm_ch4(i)=Dbch4(i)*(((rhoch4(i,Nr) - rhoch4(i,nr))/dr)./(rhoch4(i,Nr)-ych4(i)*rhobT(i)));
    hm_h2o(i)=Dbh2o(i)*((rhoh2o(i,Nr) - rhoh2o(i,nr))/dr)./(rhoh2o(i,Nr)-yh2o(i)*rhobT(i));
    hm_co(i)=Dbco(i)*((rchoco(i,Nr) - rchoco(i,nr))/dr)./(rchoco(i,Nr)-yco(i)*rhobT(i));
    hm_co2(i)=Dbco2(i)*((rchoco2(i,Nr) - rchoco2(i,nr))/dr)./(rchoco2(i,Nr)-yco2(i)*rhobT(i));
    hm_h2(i)=Dbh2(i)*((rhoh2(i,Nr) - rhoh2(i,nr))/dr)./(rhoh2(i,Nr)-yh2(i)*rhobT(i));
    Nu(i)=h(i)*(2*R)./kbT(i);
    Sh_ch4(i)=hm_ch4(i)*(2*R)./Dbch4(i);
    Sh_h2o(i)=hm_h2o(i)*(2*R)./Dbh2o(i);
    Sh_co(i)=hm_co(i)*(2*R)./Dbco(i);
    Sh_co2(i)=hm_co2(i)*(2*R)./Dbco2(i);
    Sh_h2(i)=hm_h2(i)*(2*R)./Dbh2(i);
    Re(i)=mT*(2*R)./(mubT(i)*Aflow);
    Pr(i)=cpbT(i).*mubT(i)./kbT(i);
    Sc_ch4(i)=mubT(i)./(rhobT(i).*Dbch4(i));
    Sc_h2o(i)=mubT(i)./(rhobT(i).*Dbh2o(i));
    Sc_co(i)=mubT(i)./(rhobT(i).*Dbco(i));
    Sc_co2(i)=mubT(i)./(rhobT(i).*Dbco2(i));
    Sc_h2(i)=mubT(i)./(rhobT(i).*Dbh2(i));
    InvGz(i)=(z(i)/(2*R))/(Re(i)*Pr(i));
    InvGzm_ch4(i)=(z(i)/(2*R))./(Re(i).*Sc_ch4(i));
    InvGzm_h2o(i)=(z(i)/(2*R))./(Re(i).*Sc_h2o(i));
    InvGzm_co(i)=(z(i)/(2*R))./(Re(i).*Sc_co(i));
    InvGzm_co2(i)=(z(i)/(2*R))./(Re(i).*Sc_co2(i));
    InvGzm_h2(i)=(z(i)/(2*R))./(Re(i).*Sc_h2(i));
    Taxis(i)=Temp(i,1);
    wch4axis(i)=Con_ch4(i,1);
    wh2oaxis(i)=Con_h2o(i,1);
    wcoaxis(i)=Con_co(i,1);
    wco2axis(i)=Con_co2(i,1);
    wh2axis(i)=Con_h2(i,1);
    Xch4wall(i)=molfracch4(i,Nr);
    Xh2owall(i)=molfrach2o(i,Nr);
    Xcowall(i)=molfracco(i,Nr);
    Xco2wall(i)=molfracco2(i,Nr);
    Xh2wall(i)=molfrach2(i,Nr);