A TWO-DIMENSIONAL HETEROGENEOUS NUMERICAL MODEL FOR AUTO-THERMAL REFORMING OF SYNTHETIC CRUDE GLYCEROL IN A PACKED BED TUBULAR REACTOR

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Jason McNair Williams, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *A Two-Dimensional Heterogeneous Numerical Model for Auto-Thermal Reforming of Synthetic Crude Glycerol in a Packed Bed Tubular Reactor*, in an oral examination held on Friday, July 21, 2017. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

Hydrogen (H₂) production has garnered attention amongst renewable energy researchers and intergovernmental agencies because of its potential to be an energy carrier and ability to satisfy the energy requirements of society. To date, the primary resource for H₂ production is methane (CH₄) found in natural gas, and to reduce fossil fuel utilization, other hydrocarbon sources have been identified. Glycerol is the by-product of biodiesel production, and with excess crude glycerol on the market, it proves advantageous to apply reforming methods to this feedstock to produce hydrogen.

This work presents numerical models for a catalytic auto-thermal reforming (ATR) process developed for converting synthetic crude glycerol (CG) to hydrogen gas in packed bed tubular reactor (PBTR). The models were heterogenous, considering the presence of the solid catalyst and created with two numerical methods, the finite difference method (FDM) in MATLAB and the finite element method (FEM) in COMSOL Multiphysics. Both models were validated with experimental data obtained from a laboratory-scale ATR process in the presence of a Ni-based catalyst, developed under the Advanced Green Energy Systems research portfolio at the University of Regina. The power law rate model derived from the experiments was used in the model development.

The CG conversion in the simulation data from the models were in good agreement with experimental data giving absolute average deviation (AAD) values of 7.56% and 6.34% for that created with FEM and FDM respectively. The conversion and temperature trends for the two models were compared to each other, with a previously built pseudo-
homogeneous model for this same ATR process, developed in other work. From a qualitative standpoint, the two heterogeneous models, though not aligned perfectly, trended in the same manner. At the reaction zone, the FDM model prediction gave a slightly higher bulk fluid temperature. The heterogeneous models predicted a lower reaction zone temperature by approximately 6 °C, thus showing the impact of inclusion of the heat and mass transfer at the fluid-solid interface between into the governing equations. A different approach was used in COMSOL by manipulating the modules to overcome the limitation of generating temperature profiles for the catalyst pellet. The generated profiles for the catalyst particles in FDM and FEM were also showed to be in good agreement.

Simulations were done with the FEM model varying the feed temperature from 773K to 923K and the space time from 12.71 g cat/min mol C to 158.23 g cat/min mol C. An increase in temperature resulted in increased CG conversion and H₂ yield. This was also observed as the space time increased.

Effectiveness factors were calculated using concentration and temperature profiles for the solid catalyst generated with the FDM to quantify how much of the catalyst surface is being used for the reaction. Initial simulations were done in accordance with the physical experiments at a catalyst size of 0.8 mm. Increasing the catalyst size in the simulation showed a significant difference between bulk fluid and solid catalyst temperature and concentration as species travelled along the reactor, decreasing CG conversion at the exit of the reactor, highlighting the importance of reducing the resistance to heat and mass resistance from fluid to solid.
ACKNOWLEDGEMENTS

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I also take this opportunity to express sincere gratitude to my friends Tricia, Sheena-Maria, Prince, Alia, Davia, Melodie, Howard and Trecia for their encouragement throughout this process. Finally, I thank my family, Justin Williams, Trevor Williams and especially my mother, Wendy Williams for her unwavering support whenever times got tough.
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NOMENCLATURE

$\bar{C}_i$ Dimensionless Concentration
$\bar{r}$ Dimensionless radial distance
$\bar{T}$ Dimensionless Temperature
$\bar{z}$ Dimensionless axial distance
1-D One Dimensional
2-D Two Dimensional
AAD Average absolute deviation
AHM Alternative Heterogeneous Model
ATR Auto-Thermal Reforming
$a_v$ Particle surface area to volume ratio, $m^2/m^3$
Bi Biot Number
C Concentration of species, mol/m$^3$
CG Synthetic Crude Glycerol
CH$_4$ Methane
CHM Conventional Heterogeneous Model
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>$C_{pf}$</td>
<td>Specific heat capacity of bulk fluid, kJ/J K</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Binary Diffusivity between two species, m²/s</td>
</tr>
<tr>
<td>DAE</td>
<td>Differential Algebraic Equation</td>
</tr>
<tr>
<td>Damk</td>
<td>Damkolher Number</td>
</tr>
<tr>
<td>$D_{er}$</td>
<td>Effective Radial Diffusivity in the Gas Phase, m²/s</td>
</tr>
<tr>
<td>$D_{es}$</td>
<td>Effective Diffusivity in the Solid Phase, m²/s</td>
</tr>
<tr>
<td>$D_{ez}$</td>
<td>Effective Axial Diffusivity in the Gas Phase, m²/s</td>
</tr>
<tr>
<td>$D_{im}$</td>
<td>Effective Diffusivity of a species in a mixture, m²/s</td>
</tr>
<tr>
<td>$D_{K}$</td>
<td>Knudsen Diffusivity, m²/s</td>
</tr>
<tr>
<td>$d_{p}$</td>
<td>Diameter of Catalyst particle</td>
</tr>
<tr>
<td>$D_t$</td>
<td>Reactor internal diameter, m</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation energy, J/mol</td>
</tr>
<tr>
<td>f</td>
<td>Fluid Phase</td>
</tr>
<tr>
<td>F</td>
<td>Flow rate, mol/min</td>
</tr>
<tr>
<td>FDM</td>
<td>Finite Difference Method</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>G</td>
<td>Mass Flux, kg/m²-hr</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>GUI</td>
<td>Graphical User Interface</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water/Steam</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>HET</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>$h_{fs}$</td>
<td>Effective heat transfer coefficient between solid and gas, J/s-m(^2)-K</td>
</tr>
<tr>
<td>HOM</td>
<td>Pseudo-homogeneous</td>
</tr>
<tr>
<td>$H_f$</td>
<td>Heat of formation, kJ/mol</td>
</tr>
<tr>
<td>$H_0$, $H_{rx}$</td>
<td>Heat of reaction, kJ/mol</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Frequency Factor, mol C kgcat(^{-1}) min(^{-1}) atm(^{3.5})</td>
</tr>
<tr>
<td>$k_{fs}$</td>
<td>Effective mass transfer coefficient between solid and gas, m/s</td>
</tr>
<tr>
<td>kg</td>
<td>Kilograms</td>
</tr>
<tr>
<td>L</td>
<td>Length of reactor, m</td>
</tr>
<tr>
<td>$M_{ave}$</td>
<td>Average molecular weight, kg/mol</td>
</tr>
<tr>
<td>N</td>
<td>Molar Flux, mol/s</td>
</tr>
<tr>
<td>$N_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>$O_2$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>PBTR</td>
<td>Packed Bed Reactor</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial Differential Equation</td>
</tr>
<tr>
<td>$P_{eh}$</td>
<td>Radial Fluid Heat Peclet Number</td>
</tr>
<tr>
<td>$P_{em}$</td>
<td>Radial Fluid Mass Peclet Number</td>
</tr>
<tr>
<td>$P_{eh}$</td>
<td>Axial Fluid Heat Peclet Number</td>
</tr>
<tr>
<td>$P_{em}$</td>
<td>Axial Fluid Mass Peclet Number</td>
</tr>
<tr>
<td>PO</td>
<td>Partial Oxidation</td>
</tr>
<tr>
<td>r</td>
<td>Radial Distance, m</td>
</tr>
</tbody>
</table>
R  Radius of reactor, m
Rg  Ideal Gas constant, J/mol/K
rp  Radius of Catalyst particle
s  Solid Phase
SMR  Steam Reforming
SS  Steady State
Sth  Heat Stanton Number
Stm  Mass Stanton Number
T, To, Ta  Temperature, K
u  Dummy variable
Ua  Overall Heat Transfer Coefficient, W/m^2-K
uz  Axial superficial velocity, m/s
v  Stoichiometric coefficient
V  Diffusion Volume
w  Dummy variable
W  Weight of catalyst
W/Fa  Space time, g cat min/mol C
X  Conversion
y  Mole Fraction
z  Axial distance, m
Greek Letters

\( \alpha \) Length to radius scaling factor

\( \rho_B \) Catalyst bulk density, kg/m\(^3\)

\( \rho_g \) Gas density, kg/m\(^3\)

\( \varepsilon_b \) Bulk fluid porosity

\( \varepsilon_s \) Solid pellet porosity

\( \eta \) Effectiveness Factor

\( \lambda_{er,f} \) Effective radial conductivity, J/s-m-K

\( \lambda_{es} \) Effective solid phase conductivity, J/s-m-K

\( \lambda_{ez,f} \) Effective axial conductivity, J/s-m-K

\( \mu \) Viscosity

\( \tau \) Tortuosity

\( \Phi \) Thiele Modulus
CHAPTER 1: INTRODUCTION

1.1 HYDROGEN AND ITS POTENTIAL

The provision of sustainable and affordable energy solutions for the world’s growing population poses a major challenge for governments as it is estimated that the world’s population will reach approximately 9 billion by the year 2050 (Turner et al., 2008). With the growing population, energy demands will exponentially increase, with the need for clean, sustainable sources. Because of this, hydrogen utilization for energy generation as a clean source has garnered some attention in recent times and has been the focal point of various researchers around the world to produce this form of clean energy at a competitive price, while meeting consumer needs (Kraleva, Pohl, Jürgensen, & Ehrich, 2015).

Being the most abundant element on Earth, hydrogen has been identified as a potential energy carrier because of some advantageous physical and chemical properties, most notably, its combustibility releasing a considerably high amount of energy per unit mass (-120 MJ/kg). Apart from that, it can be stored, transported and recycled. Hydrogen is utilized in the petrochemical industry fuel processing, as there is still a heavy dependence on fossil fuel utilization (Rosen & Koohi-Fayegh, 2016). Apart from the petrochemical industry, the element is used as a building block for different industrial applications such as the manufacture of fertilizers, paints, methanol, ammonia and hydrogenated vegetable oils (Sharma & Ghoshal, 2015). Figure 1-1 below gives a pictorial overview of the various pathways to Hydrogen production.

Figure 1-1: Pictorial overview of various pathways to Hydrogen production.
Figure 1-1 Pathways to Hydrogen Production and Utilization (Balat, 2008)
What is shown is the identified energy sources for hydrogen production, whether it be from fossil fuels, renewable energy or a nuclear source. The different physical, chemical and biological methods that can be used for conversion are also displayed. It is proposed that along with the existing industrial applications of hydrogen utilization, hydrogen technologies should have widespread application as a transportation fuel, as well as to be used for power generation in residential homes (Balat, 2008). The underlying cause of concern for fossil fuel utilization is due to the pollutants released into the atmosphere after combustion, including carbon monoxide, particulates, nitrous oxides which are harmful to the atmosphere, potentially having a negative impact on climate change. The outlook of hydrogen production indicates the positive global impact on the world, by challenging the fuel prices, and providing a clean transportation fuel and power source (Demirbas, 2017). Availability studies for hydrogen production in the United States have shown that there are enough renewable sources with regards to production potential to match the production of hydrogen from fossil and nuclear sources (Melaina, Penev, & Heimiller, 2013). The study done by Melaina et al. (2013) showed the production potential for hydrogen from wind, solar and biomass, based on availability across the land mass. The study showed that solar energy had the greatest availability across the region to produce hydrogen, followed by wind energy, which had a greater concentration of availability along the central region of the country. Biomass showed greater concentration in eastern regions. Despite the information displayed in the report, a broader economic study was required based on production and delivery costs.

Olateju (2016) provided a recent study of the cost of hydrogen production from renewable and non-renewable sources in Western Canada. The economic assessment
compared the cost of steam reforming of natural with wind energy, hydropower and coal. As it stands to date, natural gas steam reforming is a mature technology, which when combined with carbon-capture storage technology to reduce carbon dioxide emissions, can produce hydrogen at a low cost. Based on the models, it was determined that a hydropower operation can be a competitive alternative to steam reforming for large-scale hydrogen production, considering availability and logistics. Overall, a broader study would be required across to Canada to provide an up to date assessment on the economic viability of complete elimination of fossil fuels.

1.1.1 GLYCEROL FOR HYDROGEN PRODUCTION

Hydrogen is primarily produced from fossil fuels, with methane (CH₄) being the most prevalent feedstock (Dou, Song, Wang, Chen, & Xu, 2014; Schwengber et al., 2016). Glycerol, a by-product of biodiesel production, also provides another alternative for fossil fuel reforming. The glycerol product can be purified and sold for different applications, but as an oxygenated hydrocarbon we can utilize this to create Hydrogen gas. By 2016, it was estimated that the crude glycerol production would reach four billion gallons with further increases expected as imports to India and China increased by 35% and 30% respectively (Garlapati, Shankar, & Budhiraja, 2016). With increased glycerol production, subsequent to the demand of bio-fuels, a potential glut on the market gives us the opportunity to take advantage of the hydrogen production potential from glycerol.

As highlighted in literature, crude glycerol is toxic to the environment, containing a large amount of impurities which poses a challenge for conversion. Despite this, and the
production costs which limits the deployment of hydrogen energy technologies at a global scale, researchers project that these issues will be solved and these technologies can be introduced to developing countries within the next 20-30 years, where hydrogen and electricity will replace fossil fuels as global dominant energy carriers (Rosen & Koohi-Fayegh, 2016; Scognamiglio, 2008).

1.2 MOTIVATION

1.2.1 PROBLEM STATEMENT

Experiments have been performed at the University of Regina by Abdul Ghani (2014), to produce hydrogen rich syngas, in a PBTR, via the ATR of synthetic crude glycerol. After obtaining a kinetic rate expression for the system from the baseline experiments, it proves beneficial to transition to a simulation environment. This is because results can be reproduced at a lower cost and faster rate.

The power law rate model developed by Abdul Ghani (2014) was utilized in a pseudo-homogeneous model done by Afabor (2015). The pseudo-homogeneous model does not explicitly account for the presence of the catalyst particles, providing an opportunity to include heterogeneity into the model.

The software platforms used for reactor modelling have human -interfaces allow users to enter input parameters, while calculations are performed in the background. Recent versions of COMSOL Multiphysics, offer a Reactive Pellet Module catered to the heterogeneous model development, for mass transfer only. It is also noted that for ATR, past modelling research by Allain et al. (2010) and Dixon et al. (2014) utilized the
general extrusion coupling feature to simulate both mass and energy in the catalyst pellet, but the opportunity exists to develop a more innovative configuration in COMSOL Multiphysics to develop a comprehensive heterogeneous reactor model.

1.3 OBJECTIVES

After review of recent literature, the purpose of this thesis is to develop a two-dimensional (2-D) heterogeneous, comprehensive reactor model for a PBTR, simulating the ATR of synthetic crude glycerol. The models will be developed using two numerical methods, the Finite Difference Method (FDM) and the Finite Element Method (FEM).

The thesis will be broken down into three different phases. Phase I will be the development of the reactor model with the FEM with COMSOL Multiphysics software. Phase II will be the development of the model with a custom code. The FDM model will be developed with a custom code using MATLAB software. The two models will be validated with experimental data and be compared with a previously built pseudo-homogeneous model. Sub-models for mass, energy and consideration for momentum along the reactor tube will be performed, as well as a sub-model for interactions within the catalyst pellet. Phase III will be investigating the possible scale-up to a hypothetical industrial reformer. To date, there is no commercial process which exists for the ATR of synthetic crude glycerol in a PBTR.
1.4 ORIGINAL CONTRIBUTIONS

Modelling can be developed with both commercial software packages and custom coding developed with a programming software such as C++ or FORTRAN. The commercial software package can be more user friendly with its associated interface, and may require less effort. On the other hand, custom coding can produce similar results, and with a lower cost to that of a commercial software.

This work presents two models developed for the ATR of synthetic crude glycerol in a PBTR explicitly accounting for the presence of the solid catalyst phase. The first model is to be developed with an in-house developed in MATLAB, and secondly with COMSOL Multiphysics. The development of a robust model can prove beneficial to the overall reactor design.
CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

Glycerol is the main by-product from the production of biodiesel, and as the market for biodiesel continues to grow, then there will be a subsequent increase in the production of glycerol. Logically, we will need to develop ways to utilize the glycerol generated to create value added products (Thompson & He, 2006; Vaidya & Rodrigues, 2009). Glycerol has application in industries such as food and beverage, personal and oral care and tobacco; as well as some research surrounding the use of glycerol as an additive for gasoline blending. Because of the characteristics of hydrogen gas, it has become a focal point for clean energy technologies.

It is given that for every gallon of biodiesel produced by an operating facility, approximately 1.05 pounds of glycerol can be produced. However, despite glycerol being a valuable product with extensive commercial potential, purification can be expensive (Yang, Hanna, & Sun, 2012). To eliminate to production costs associated with glycerol production, it is proposed to utilize the crude glycerol and prevent it from going to waste.

Crude glycerol is a highly toxic and corrosive material due to the impurities present and previous analysis shows that the composition of crude glycerol can vary with efficiency of the biodiesel production process, as well as the impurities in the feedstock (Abdul Ghani, 2014; Yang et al., 2012). It can consist of glycerol, methanol, soap, potassium hydroxide. Yang et al. (2012) reported on the collection of samples from Australian biodiesel producers who utilized sunflower oil and reported compositions in (w/w%) of 30% glycerol, 50% methanol, 13% soap, 2% moisture and 2% potassium and sodium.
salts. The ATR process developed by Abdul Ghani (2014) utilized a synthetic feed prepared by mixing various components generally found in a crude generated by a biodiesel plant. The components of this crude are given in Appendix A.

Overall, research has proven that crude glycerol can be as valuable as the purified glycerol, with a variety of opportunities being identified and listed below (Chethan, 2014):

- Utilization in animal feed
- Feedstock for chemicals
  - 1,3-propanediol
  - Hydrogen
  - Citric Acid
  - Ethanol
  - Methane
  - Butanol
  - Lipase

Converting the glycerol into these products can only prove to be advantageous as it allows for control of any market surplus of crude glycerol which can occur, as well as offset biodiesel production costs.
2.2 REFORMING METHODS

Some of the chemical conversion methods researched for hydrogen production include (Adhikari, Fernando, & Haryanto, 2009):

- Steam Reforming
- Partial Oxidation
- Auto-thermal Reforming
- Aqueous-Phase Reforming
- Supercritical Water Reforming

Extensive literature has been written on each of these methods with the focus of this work being the modelling of an Auto-thermal Reforming (ATR) process which is the combination of Steam Reforming (SMR) and Partial Oxidation (PO).

2.2.1 STEAM REFORMING

Steam Reforming (SMR) of Hydrocarbons, primarily with methane, is the original thermochemical process used to produce Hydrogen. There can also steam reforming performed with alternative feedstocks such as ethanol or butanol (Baruah, Dixit, Basarkar, Parikh, & Bhargav, 2015). Ethanol has been by governments for gasoline blending, but in a surplus on the market, this could be a used as a feedstock. Due to the potential surplus of glycerol being produced, glycerol is used as the feedstock for steam reforming with the following overall reaction that is endothermic in nature. A typical reaction for the SMR of glycerol can be given as:
\[ \text{C}_3\text{H}_8\text{O}_3 + 3\text{H}_2\text{O(g)} \rightarrow 3\text{CO}_2 + 7\text{H}_2 \quad \Delta H^\circ = 123 \text{ kJ/mol} \]  \hspace{1cm} (2.1)

In literature, the overall reaction is a combination of two reactions, glycerol decomposition (2.2) and a water gas shift (2.3) (Sad et al, 2015).

\[ \text{C}_3\text{H}_8\text{O}_3 \rightleftharpoons 3\text{CO} + 4\text{H}_2 \quad \Delta H^\circ = 245 \text{ kJ/mol} \]  \hspace{1cm} (2.2)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -41 \text{ kJ/mol} \]  \hspace{1cm} (2.3)

The formation of CO and H\(_2\) is also dependent on the presence of a catalyst and reaction conditions.

### 2.2.2 PARTIAL OXIDATION

Partial Oxidation (PO) has its advantages as self-sustaining process under ambient pressure. It was first pioneered utilizing Pt and Rh-based catalysts as the process was first considered for its theoretical energy efficiency and simplicity Abdul Ghani (2014). It is preferred over SMR in situations, where a small-scale operation is required, where the priority is not efficiency, as it has been shown in studies that PO may not produce hydrogen yields compared to SMR (Welaya, El Gohary, & Ammar, 2012).

The typical reaction for PO of crude glycerol is as follows (Vaidya et al, 2009):

\[ \text{C}_3\text{H}_8\text{O}_3 + \frac{3}{2} \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2 \quad \Delta H^\circ = -603 \text{ kJ/mol} \]  \hspace{1cm} (2.4)

Compared to steam reforming, it’s also possible to manipulate the production of syngas with variations in the amount of oxygen in the input. Due to the exothermic nature of the process, lack of understanding of the reactions parameters for partial oxidation can
produce several side reactions producing carbon monoxide, methane and coke (carbon) which are undesirable.

2.2.3 AUTO-THERMAL REFORMING (ATR)

Auto-thermal reforming (ATR) is a combination of steam reforming and partial oxidation. An example of the reaction for this process can be presented as (Fan, Burton, & Zhou, 2010):

\[ C_3H_8O_3 + \frac{3}{2}H_2O + \frac{3}{4}O_2 \rightarrow 3CO_2 + \frac{11}{2}H_2 \quad \Delta H^o = -240 \text{ kJ/mol} \quad (2.5) \]

This process is touted for being ‘self-sustaining’ with regards to energy requirements. This is because the exothermic nature partial oxidation reaction generates heat which is absorbed by the steam reforming process. Conceptually, no external energy should be required to produce hydrogen and high H\textsubscript{2} yield should be obtained.

Studies associated with the ATR of methane done by Dauenhauer et al. (2006) showed that at high steam-to-carbon (SC) ratios resulted in favorable Hydrogen selectivity and yield. Other studies showed that temperatures in the range of 500\textdegree C to 800\textdegree C, and under atmospheric pressure, hydrogen yields were higher than those observed with Steam reforming. These studies were all predicated on the selection of the appropriate catalyst.

2.3 REACTOR MODELLING

When modelling the reactor, our aim is to reproduce virtual results that the reactor would physically produce minus the cost associated with physical experiments. For a tubular
packed bed reactor, the general equations for mass, energy and momentum can be expressed in terms of the weight can be given as (Fogler, 2011; Hill & Root, 2014):

\[
\frac{dX}{dW} = -\frac{r_A}{F_{A0}} \\
\frac{dT}{dW} = -\frac{r_A \Delta H_{rx}(T) - \frac{U_a}{\rho_b} (T-T_A)}{F_A \rho_f} \\
\frac{dP}{dW} = -\frac{G}{\rho g c_p D_p} \left(\frac{1-\varepsilon_b}{\varepsilon_b^3}\right) \left[\frac{150(1-\varepsilon_b) \mu}{D_p} + 1.75G\right]
\]

In these equations $X$ is the conversion in the reactor, $W$ is the weight of the catalyst, kg; $r_A$ is the rate of reaction of an arbitrary species A, mol/kg cat s; $\Delta H_{rx}$ is the Heat of Reaction, J/mol; $U_a$ is the overall heat transfer coefficient W/m$^2$-K; $T$ is the temperature in the reactor, K; $T_A$ is the ambient air temperature, K; $F_A$ is the flow rate m$^3$/s; $P$ is the pressure, Pa; $C_p$ is the specific heat capacity kJ/kg-K; $G$ is the Mass Flux; kg/s-m$^2$; $\rho_f$ is the fluid density kg/m$^3$. $\varepsilon_b$ is the void fraction of the catalyst bed.

Depending on the detail of design required, engineers may opt to have more comprehensive equations for these three properties. Figure 2-1 is a pictorial of the mechanisms that occur within the PBTR which can be considered for modelling.
Figure 2-1 Transport Phenomena Mechanisms in Packed Bed Reactor

1. Bulk Fluid Flow
2. Axial Diffusion and Conduction
3. Fluid to Solid Heat Transfer
4. Fluid to Solid Mass Transfer
5. Solid to Wall Heat Transfer
6. Fluid to Wall Heat Transfer
7. Chemical Reaction
8. Pore Diffusion
9. Solid Axial Conduction
10. Solid Radial Conduction
11. Radial Diffusion and Conduction
12. Velocity Distribution
Froment et al. (2011) categorized reactor models into two broad categories, those being heterogeneous (HET) and pseudo-homogeneous (HOM). They describe the most basic model for a fixed bed reactor model to be a pseudo-homogeneous one-dimensional (1-D) model plug flow model. With this basic model, temperature and concentration gradients are accounted for only in the axial direction. The model can be extended to become two-dimensional (2-D), accounting for gradients that could occur in the radial direction; and then for a heterogeneous model, transport phenomena within the catalyst is investigated (Ding & Chan, 2008).

Complexity may be a matter of the desire of the researcher, as it may not always be required. The features of a process including a fixed bed reactor can provide a challenge in modelling such as (Ding & Chan, 2008; He, 2003):

1. The presence of two phases
2. Nonlinear reaction rates impacted by both concentration and temperature.
3. Various reaction schemes that occur within the reactor bed
4. Random distribution of the catalyst particles which may affect fluid flow.

### 2.4 PACKED BED REACTOR MODELS AND SIMULATION

Several models have been developed in previous years which can simulate chemical processes requiring a packed bed reactor. This section we will highlight different types of models developed by various authors.

He (2003) studied the partial oxidation of ortho-xylene in a of a fixed bed reactor using pseudo-homogeneous and heterogeneous transient models, with one of the objectives to
compare the results obtained by the two approaches. The dissertation by He (2003) included optimization methods for parameter estimation of two kinetic models and their suitability to the approaches generated. The model was developed in FORTRAN with an ‘in-house’ DAE solver, with the equations for mass and energy discretized with FDM. The solver was shown to be efficient in solving the transient equations developed.

Rout et al. (2015) provided a comprehensive study comparing different types of numerical modelling for a packed bed reactor model. They compared pseudo-homogeneous and heterogeneous models for an SMR process. Studies of the heterogeneous models were further divided into the conventional and the simplified approach, which assesses diffusional limitations by calculating effectiveness factors. At different positions along the reactor length. The method of weighted residuals with collocation was employed to model a steady state (SS) SMR process. The models were acceptable, however, Rout et al. (2015) also suggested the use of the conventional heterogeneous model, to avoid the use of a changing effectiveness factor.

Ghouse et al. (2013) developed a two-dimensional heterogeneous transient model for a SMR process. The model was validated with industrial steady-state data from literature, with temperature and concentration gradients inside the catalyst being evaluated along the reactor length (De Deken, Devos, & Froment, 1982; Soliman, El-Nashaie, Al-Ubaid, & Adris, 1988; Xu & Froment, 1989). The simulation was performed using the software gPROMS, with the Partial Differential Equations (PDE) and Differential Algebraic Equations(DAE) discretized with FDM. The temperature variations between tube wall and catalyst were accounted for in this study.
A mathematic model for the ATR of Methane developed by Rowshanzamir et al. (2009) using FDM. The model developed was for a one-dimensional (1-D) heterogeneous system and displayed an acceptable agreement to experimental data. Temperature and concentration profiles were developed and predicted using the relevant conversation equations with a kinetic model developed from 108 elementary reactions.

Scognamiglio et al. (2012) also simulated a catalytic ATR process utilizing a Rhodium catalyst by developing a one-dimensional, steady state, heterogeneous model for an adiabatic system. The PDEs for this model were developed for both mass and energy, assuming ideal gas conditions. As done in previous models, momentum was accounted for with use of the Ergun equation which calculates the pressure drop in the reactor. Using the equations will usually come with the assumption of a constant velocity across the reactor. The overall system of equations consisting of DAEs and algebraic equations were discretized with FDM solved using the software Mathematica. For all operating conditions considered in the study, the model was deemed accurate. The catalyst bed is fixed in the reactor tube between two sets of inert pellets, proposedly to assist with reactor mixing and feed preheating. This model primarily investigated the effects of thermal conductivity in the catalyst bed and flow rate on the generated predictions for this model.

Dixon et al. (2014) modelled hydrogen production by the SMR of both glycerol and methane. The one-dimensional, heterogeneous model was done with COMSOL Multiphysics software with utilizes the FEM, with mass and momentum being modelled. The model accounted for a change in density and velocity by the pressure drop calculated by the Ergun equation. The main purpose of the study was to understand the mole
changes which will occur for an isothermal operation. Although they saw a change in the velocity due to a pressure drop, conversion of Glycerol was unaffected by this pressure drop, unlike that seen for the SMR of methane, this would have been attributed to the length of reactor being 10m, while a 1m length reactor was used for SMR of glycerol.

A heterogeneous model developed by Avci et al. (2001), simulated the ATR of methane. Both industrial and laboratory scale packed bed configurations were simulated to assess the optimum operating conditions necessary for maximizing hydrogen production. The model equations were one-dimensional and executed using ODE solvers in MATLAB using a least-squares technique combined with Gauss-Newton methods. The model worked successfully for after scaling up from bench-scale to an ‘industrial’ simulation, also noting that there was a significant pressure drop was observed for the industrial scale.

### 2.4.1 SUMMARY OF MODELS IN LITERAURE

In this section, the tables give a summary of various models described in literature as it pertains to PBTR modelling, not limited to hydrogen production. The approach in these models were all not identical with variances described by Froment et al. (2011) from steady state (SS) to dynamic (DYN)/transient state models, and from one dimensional (1-D) to two dimensional (2-D).
<table>
<thead>
<tr>
<th>Author</th>
<th>Scope</th>
<th>Computational Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Chan, Hoang, &amp; Ding, 2005)</td>
<td>Dynamic Modelling of ATR of Methane for predicting dynamic responses with flow rate pulses; 2-D HET, DYN</td>
<td>FDM</td>
<td>Effectiveness Factors were utilized in the modelling equations. Compared to previous steady state models using the same dimensions and conditions, conversion of reactants to products followed similar trend to previous models but were slightly underpredicted</td>
</tr>
<tr>
<td>(Aboudheir, Akande, Idem, &amp; Dalai, 2006)</td>
<td>PBTR steady state modelling study for reforming of crude ethanol comparing lab scale to industrial data; 2-D HOM, SS</td>
<td>FEM in COMSOL</td>
<td>Model provided acceptable predictions. It was noted that momentum balances should have been solved for industrial scale data where deviation from plug flow was possible</td>
</tr>
<tr>
<td>(Wesenberg &amp; Svendsen, 2007)</td>
<td>Steady state SMR of Methane in a reactor with a fixed bed in shell-tube configuration; 2-D HET, SS</td>
<td>FDM in PRO/II</td>
<td>Determined the significance of accounting for particle-fluid transport limitations</td>
</tr>
<tr>
<td>(Quina, Almeida-Costa, &amp; Quinta-Ferreira, 2007)</td>
<td>Simulation of Partial Oxidation of two case studies of Synthesis of Phthalic Anhydride and Synthesis of Formaldehyde; 1-D, 2-D, HET SS</td>
<td>FDM/OC, FORTRAN</td>
<td>Compared the results between the complexity of heterogenous models by including radial and axial transport coefficients for mass and heat</td>
</tr>
<tr>
<td>(Halabi, De Croon, Van der Schaaf, Cobden, &amp; Schouten, 2008a)</td>
<td>Modelling of ATR of Methane under bench-scale conditions; 1-D HET, DYN and SS</td>
<td>Backward FDM in gPROMS</td>
<td>Effectiveness Factors utilized and optimal operating ranges identified for maximizing Methane conversion</td>
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<td>Author</td>
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<tr>
<td>(Scognamiglio, 2008)</td>
<td>Modelling of Temperature Profiles for ATR of Methane; 1-D HET, SS</td>
<td>FDM in Mathematica</td>
<td>Model was deemed accurate for predicting methane conversion compared to experimental values</td>
</tr>
<tr>
<td>(Oliveira, Grande, &amp; Rodrigues, 2009)</td>
<td>Simulation for SMR of Methane; 1-D HET, SS</td>
<td>Central FDM in gPROMS</td>
<td>Non-isothermal model developed for catalyst particle to evaluate diffusion effects and thermal gradients within particle</td>
</tr>
<tr>
<td>(Varela &amp; Garcia, 2009)</td>
<td>Simulation of Phthalic Anhydride synthesis; 2-D HET, SS</td>
<td>FEM in COMSOL</td>
<td>Significant differences in catalyst temperature and bulk fluid based on operating conditions of simulation</td>
</tr>
<tr>
<td>(Manenti, Cieri, &amp; Restelli, 2011)</td>
<td>Steady State Modelling comparing the effectiveness of two different type of mathematical models for predicting Methanol synthesis in a shell and tube boiler reactors; 1-D HET and 1-D HOM, SS</td>
<td>C++</td>
<td>The heterogeneous and pseudo-homogeneous models show similar results. Proposed use of the pseudo-homogeneous model to reduce computational effort</td>
</tr>
<tr>
<td>Scognamiglio et al, 2012</td>
<td>Kinetic and Steady State modelling for ATR of Methane in bench scale reactor; 1-D HET, SS</td>
<td>FDM in Mathematica</td>
<td>Model was deemed accurate for predicting methane conversion compared to experimental values</td>
</tr>
<tr>
<td>(Sadooghi &amp; Rauch, 2013)</td>
<td>Heterogeneous Modelling for SMR of Methane to Syngas for a bench scaled reactor; 2-D HET, SS</td>
<td>FEM in COMSOL</td>
<td>Determined radial gradients are negligible. Mathematical model deemed acceptable</td>
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<tr>
<td>(Petera, Nowicki, &amp; Ledakowicz, 2013)</td>
<td>A heterogeneous model simulating Methanol Synthesis coupling micro- and macro geometries; 2-D HET, DYN</td>
<td>FEM in COMSOL</td>
<td>Temperature and concentration profiles modelled with potential spot conditions identified</td>
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<td>Author</td>
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<tr>
<td>(Ghouse &amp; Adams, 2013)</td>
<td>2-D Heterogeneous model for SMR of Methane; 2-D HET, DYN</td>
<td>FDM in gPROMS</td>
<td>Model validated with steady state data from literature. Effectiveness factor used to account for diffusional limitations.</td>
</tr>
<tr>
<td>(Ghavipour &amp; Bebbahani, 2014)</td>
<td>Unsteady state modelling of Methanol to Dimethyl Ether under adiabatic and non-adiabatic conditions; 1-D HET, SS</td>
<td>FDM</td>
<td>An empirical rate model was developed from previous literature due to deviations occurring at the desired operating conditions with previous developed rate models</td>
</tr>
<tr>
<td>(Schlereth &amp; Hinrichsen, 2014)</td>
<td>Methanation of CO₂ with an externally cooled PBTR followed by modelling with a packed bed membrane reactor; 1-D HET and 1-D HOM, SS</td>
<td>FDM in MATLAB and FEM in COMSOL</td>
<td>Pseudo homogeneous and Heterogeneous models were compared to assess the need for added complexity of fluid-particle interactions. Stability of operations to prevent runaway conditions investigated.</td>
</tr>
<tr>
<td>(Asensio, Zambon, Mazza, &amp; Barreto, 2014)</td>
<td>Fixed Bed Reactor Modelling using CFD to evaluate Fluid-Convection parameters,</td>
<td>N/A</td>
<td>Temperature predictions were compared at different tube to particle diameter ratios</td>
</tr>
<tr>
<td>(Roohi, Alizadeh, Fatehifar, &amp; Salami Hosseini, 2014)</td>
<td>Modelling of Multitubular Fixed Bed Reactor; 2-D, SS</td>
<td>FEM and FDM in MATLAB</td>
<td>The author sought to compare FEM with FDM to produce a model to produce steady state temperature and partial pressure profiles. The R² squared analysis indicated the FEM was acceptable to produce the desired model</td>
</tr>
<tr>
<td>(MacDonald, 2014)</td>
<td>Modelling and simulation of SMR in Glycerol; 1-D, HET</td>
<td>FEM in COMSOL</td>
<td>Model agreement was deemed acceptable and optimal conditions specified</td>
</tr>
<tr>
<td>(Benguerba, Dehimi, Virginie, Dumas, &amp; Ernst, 2015)</td>
<td>Dry Reforming of Methane over a Ni-based catalyst; 1-D HET, SS</td>
<td>N/A</td>
<td>Concentration and Temperature profiles obtained for bench scaled reactor.</td>
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<tr>
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<td>Computational Method</td>
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<tr>
<td>(Bakhtiari et al., 2015)</td>
<td>Kinetic and Steady State Modelling for SMR of Oxygenated hydrocarbons in PBTR with three different kinetic models; 2-D HOM, SS</td>
<td>FDM with FORTRAN</td>
<td>Maximum conversion of Glycerol occurred less than half the distance of the reactor at the desired operating conditions with the reactor operating isothermally.</td>
</tr>
<tr>
<td>(Tang, Greenwood, &amp; Erickson, 2015)</td>
<td>SMR and ATR of Methane in presence of a Copper based catalyst with pilot plant reactor; 2-D HET, SS</td>
<td>FEM in COMSOL</td>
<td>Length to Diameter ratio of reactor varied to examine its effect on conversion, leading to determination of total length required for complete conversion of Methane</td>
</tr>
<tr>
<td>(Farsi, Eslamloueyan, &amp; Jahanmiri, 2011)</td>
<td>Simulation and Control of Dimethyl Ether synthesis with an industrial sized reactor using PID feedback control to handle disturbances while maintaining inlet conditions; 1-D HET, DYN</td>
<td>FDM</td>
<td>Obtained acceptable agreement between the simulation and plant data, and the PID capable of handling disturbances.</td>
</tr>
<tr>
<td>(Cipitì et al., 2016)</td>
<td>Mathematical Model of Biogas in a non-isothermal PBTR; 1-D HOM, SS</td>
<td>FEM</td>
<td>Modelling equations modelled based on volume not axial or radial directions. Effectiveness factors considered</td>
</tr>
<tr>
<td>(Huang, Li, Li, &amp; Xiao, 2016)</td>
<td>Multiscale modelling for conversion of Methanol to Propylene validated against laboratory experimental data; 1-D HET, SS</td>
<td>FEM in COMSOL/ ODE solver in MATLAB</td>
<td>Model deemed acceptable. Intraparticle Diffusion resistance found to be factor in affecting product selectivity</td>
</tr>
<tr>
<td>(Saw, Nandong, &amp; Ghosh, 2016)</td>
<td>Kinetic Modelling and Simulation of in a PBTR for a Water Gas Shift Reaction. Macro and Micro Kinetic models compared; 1-D HOM, 1-D HET, DYN</td>
<td>N/A</td>
<td>Micro Kinetic Models gave more accurate prediction but Micro-Kinetic preferred for industry process.</td>
</tr>
<tr>
<td>Azarhoosh, Ebrahim &amp; Pourtarah 2016)</td>
<td>Simulation and Optimization of ATR of Methane and Methanol Synthesis using Industrial Data; 1-D HET, SS</td>
<td>FDM in MATLAB</td>
<td>Simulations validated by experimental data and literature</td>
</tr>
<tr>
<td><strong>Author</strong></td>
<td><strong>Scope</strong></td>
<td><strong>Computational Method</strong></td>
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<tr>
<td>(Nawaz, 2016)</td>
<td>Simulation of Industrial Packed-Bed Ethylene Oxide Reactor with optimization for maximum OE selectivity; 1-D HET, SS</td>
<td>Aspen Custom Modeler</td>
<td>Model agreement was deemed acceptable and optimization provided safe operational conditions</td>
</tr>
<tr>
<td>(Rúa &amp; Hernández, 2016)</td>
<td>Evaluating Industrial Scale SMR or Glycerol under adiabatic conditions with two different catalyst shapes; 1-D, HET, SS</td>
<td>FEM in COMSOL</td>
<td>Mass transfer inside the catalyst have found to limit the production of glycerol, with temperature gradients inside the catalyst considered negligible</td>
</tr>
<tr>
<td>(Gómez, Mmbaga, Hayes, Toledo, &amp; Gracia, 2016)</td>
<td>Simulation of Heavy Fuel Oil Combustion to produce Hydrogen; 1-D HET, SS</td>
<td>FEM in COMSOL</td>
<td>Model produce acceptable results compared to experimental data.</td>
</tr>
<tr>
<td>(Azarpour, Borhani, Alwi, Manan, &amp; Mutalib, 2017)</td>
<td>PBTR modelling study incorporating an artificial neural network to account for catalyst deactivation; 2-D HOM DYN</td>
<td>FDM</td>
<td>The model uses the neural network to create a kinetic model that includes the catalyst deactivation and produces acceptable predictions</td>
</tr>
<tr>
<td>(Azarpour et al., 2017)</td>
<td>Kinetic and Steady State Modelling for SMR coupled with WGS of Methane in Adiabatic PBTR; 1-D HET, SS</td>
<td>Backward FDM in gPROMS.</td>
<td>Discrete Model with effectiveness factor evaluated, Optimum parameters for H2 production evaluated</td>
</tr>
<tr>
<td>(Ducamp, Bengaouer, &amp; Baurens, 2017)</td>
<td>Modelling of CO₂ Methanation in an Annular Fixed Bed Reactor. 2-D HET, SS</td>
<td>FEM in COMSOL</td>
<td>Simulation developed to consider mass, heat and momentum. Diffusion limitations within the catalyst were evaluated, as well as reaction efficiency.</td>
</tr>
<tr>
<td>(Spallina, Marinello, Gallucci, Romano, &amp; Annaland, 2017)</td>
<td>PBTR model for a Chemical Loop Reforming process for H₂ production 1-D HET, DYN</td>
<td>FDM</td>
<td>The model was validated against experimental data, with thermal profiles adequately accounting for heat losses within the system.</td>
</tr>
</tbody>
</table>
2.5 NUMERICAL METHODS

Solving the equations to simulate transport phenomena within a PBTR can pose challenges with computational demands. By attempting to consider the relevant physical profiles and complexity of the desired model, we may be constrained by numerical techniques.

Packed bed reactor models are defined by a system of PDEs or algebraic equations, which can have a nonlinear reaction term. A typical PDE with a first order reaction can be solved using the Thomas algorithm, which generates a block diagonal matrix, with an iterative technique such as the Gauss-Seidel method (Chapra & Canale, 2015; Hoffman & Frankel, 2001). Finlayson (2012) gave a quasi-Newton technique, incorporating the Thomas algorithm for first and second order kinetic rate terms, utilizing various numerical techniques. Discretization techniques can create an extensive number of PDEs which can introduce several challenges with a desired numerical solution. Typical problems that have been presented in literature involve (He, 2003; Windes, 1986):

1. Stiffness which is created by the different times of the physical processes within a reaction-diffusion process.
2. Handling of the complexity of the transport models
3. The large number of equations to be solved
4. Sparsity requirements
5. Coupling of physical quantities (temperature, concentration, pressure, velocity)

Different commercial packages have been developed in recent times that can handle the scenarios listed above that can be a constraint for deriving a numerical solution in an efficient manner (Wade, 1999). These packages contain subroutines that are tailored to
solving PDEs and DAEs, with the appropriate discretization technique. The advent of more powerful computer processors, which are more compact in size and easier to manage have benefited researchers in developing the models by reducing the computational time.

2.6 CONCEPT OF THE EFFECTIVENESS FACTOR

For heterogeneous catalytic reactions, we theorize that the reactions occur on the catalyst surface and within the pores of the catalyst. By experimentation it was discovered that a resistance to heat and mass can develop which can inhibit reaction rates, which can be quantified by the Effectiveness factor (Fogler, 2011; Levenspiel, 1999). The effectiveness factor $\eta$, can be described with the following relationship:

\[
\eta = \frac{\text{actual reaction rate within the pore of catalyst particle}}{\text{reaction rate if interior particle surface is evaluated according to surface conditions with no diffusion}}
\]  

(2.9)

The effectiveness factor provides a method for accounting intraparticle resistances without having to solve a complete heterogeneous model which can improve the computational efficiency of the solver (Adagiri, Babagana, & Susu, 2012; Iordanidi, 2002). The value of $\eta$ can be influenced by the reactor shapes and its dimensions.
Figure 2-2 Effectiveness Factor vs Thiele Modulus for various reactor geometries for a first order reaction (Levenspiel, 1999)
Because of simplicity, analytical solutions for a first, second and zero order rate term have been determined and relationships between Thiele Modulus, $\phi$ and $\eta$ have been derived and shown below for reactions occurring on different catalyst geometries. Figure 2-2 above shows that for a first order reaction, we can define regions of diffusion or reaction limitation which can indicate the extent to which the catalyst pellet is contributing to the reaction. Typical values for $\eta$ will vary for 0 to 1, but it not unusual for the values to be higher. The effectiveness factor between 0 and 1 serves as an indicator to the researcher provides an indication of the percentage of how much the catalyst particle surface is being used for the reaction.

For more complex rate expressions, an analytical solution for $\eta$ may prove difficult, therefore, a numerical method can be implemented to find appropriate values for intra-pellet behavior. Kim et al. (2004) computed an effectiveness factor for a non-isothermal and isothermal catalyst particle using an initial volume shooting method, capable of providing a numerical solution for spherical and cylindrical pellets and simple or complex kinetic expressions.

Lee et al. (2004) performed steam reforming experiments over a copper-based catalyst to establish kinetics and the effectiveness factor for power-law and Langmuir-Hinselwood kinetic rate expressions. A numerical solution was developed in FORTRAN with an assumption that the catalyst particle was isothermal.

Nam (2015) also performed a comprehensive study to determine correlations for catalyst pellets with a spherical geometry in a bench scale reformer for Methane steam reforming. In conjunction with data from Baek et al. (2014), the study showed the effect of various
operating parameters such as S/C ratio and methane conversion on the effectiveness factor, using the data to develop a correlation between $\eta$ and $\phi$, with $\phi$ being a function of catalyst diameter, pore diameter, S/C ratio and the operating temperature and pressure of the system.

Hallac et al. (2015) performed optimization studies for an iron Fischer-Tropsch catalyst design, to understand the effect of the operational parameters of the heat and mass transport correlations within a catalyst. Pressure, temperature, and pellet size were varied as part of the simulation which was laboratory scale operation, as well as a commercial scale. Their experiments gave a threshold for the pellet size below which there was no diffusion limitation within the catalyst pores.

The analytical solutions for first, second order reactions provide a straightforward solution for $\eta$ in reactor modelling and reduce any potential computational demand that arises in applying a numerical method to evaluate $\eta$ at different positions along the reactor (Rawlings & Ekerdt, 2002).
Figure 2-3 Effectiveness Factor vs Thiele Modulus for various reactor geometries for a first order reaction (Levenspiel, 1999)
The figure above shows a similar characteristic shape for a reaction orders greater than one, which helps researchers to utilize correlations to approximate intra-pellet diffusion. As for the case of an isothermal spherical particle, the differential equation for a diffusion into the particle can be solved to give the solution (Davis & Davis, 2012):

\[ \eta = \frac{3}{\Phi} (\Phi \coth (\Phi-1)) \]  

Although this equation applies to a first order reaction, it has been used in model for estimation. In some cases, the effectiveness factors can be greater than one when reactions are highly exothermic. In these cases, the temperature gradients within the particle can be pronounced, which has been explained that the temperature at the surface will be less than within the particle.
3.1 INTRODUCTION

Simulating the potential performance of a reactor, the relevant mathematical equations must be used with key parameters obtained from experimental results. For a PBTR, profiles of concentration, temperature and velocity can be described by multi-dimensional PDEs which for energy, mass and momentum in transient or steady-state models.

A comprehensive model can prove to be challenging due dependent on complexities introduced. This can include the introduction of different phases, complex fluid flow patterns, mixing, random porosity distribution and utilizing correlations for transport correlations (Froment et al., 2011). In addition, there is the constraint of computational efficiency which can prevent convergence to a solution (He, 2003). In modern times, the processing power of computers have immensely improved reducing runtime of models, allowing for a more expansive scope when simulating reactors.

For this work, two approaches that are described in literature are being examined, the first which will be described as the Conventional Heterogeneous Model (CHM) and the second will be described as the Alternative Heterogeneous Model (AHM). Both versions of the heterogeneous models are used extensively in literature and the results have been comparable (Iordanidi, 2002; Park, 1995; Rout & Jakobsen, 2015). The AHM model incorporates the Effectiveness factor, $\eta$ which can provide a single figure that
determines the impact to which diffusion and conduction with the catalyst particle contributes to the conversion of products and reactants.

The modelling equations were developed and solved over a cross section of the PBTR geometry, with the continuity equations for mass, energy expressed in the radial (r) and axial(z) directions. As shown in Figure 3-1, the ‘macro’ 2-D domain is discretized to create a mesh where each node, linked by the appropriate boundary conditions, a ‘micro’ 1-D mesh is developed to represent the catalyst particle.
Figure 3-1 Schematics of the Cross-Section of the Packed Bed Reactor (Petera et al., 2013)
3.2 MODEL ASSUMPTIONS

Assumptions made in the derivation of the numerical models are:

1) The continuity equations being used for this model are implemented for cylindrical coordinates, neglecting angular variations, making it two dimensional. As it is shown, the reactor tube is represented as rectangular domain.

2) The models will be steady state to reflect the continuous operation of ‘real world’ reactor.

3) The feed mixture entering the reactor is at elevated temperature (greater than 773 K) and at atmospheric pressure. Under these conditions of temperature and pressure, intermolecular interactions are small and the feed mixture is assumed to behave as an ideal gas (Levenspiel, 1999; Scognamiglio, 2008).

4) Thermo-physical properties such as conductivity, diffusivity and viscosity of the feed mixture are assumed constant, with change of temperature in the reactor. as the species entering the reactor are considered dilute (He, 2003).

5) The axial velocity is assumed to be constant equal to the inlet velocity. Experiments done by Abdul Ghani (2014) were performed under plug flow based on the criteria that the ratio of catalyst bed length to particle diameter (L/d_p) and the ratio of was greater than or equal to 50, and the ratio of the internal reactor diameter to particle diameter is greater than or equal to 10. The L/dp and d/dp ratios were 56.3 and 15.9 respectively. To characterize flow in a porous media, extended versions on the Navier- Stokes equations such as Brinkman or Darcy have been utilized (Chabot, Guilet, Cognet, & Gourdon, 2015), however, to reduce the computational load, the constant velocity will be used for the models in this work.
6) Under plug flow criterion, dispersion in the radial direction is dominant over convective flux, making radial convection terms for both heat and mass negligible.

### 3.3 MODEL EQUATIONS

The equations used for this work consist of a set of PDEs, which are coupled across two separate domains to describe the concentration and temperature in a reactor and within a catalyst pellet. As stated in the objectives, the two numerical methods for Finite Element and Finite Difference will be used to develop the model. For simple kinetic terms which can be first or second order, analytical solution can be derived. Examples of this were shown by Rawlings et al. (2002) and Hill et al. (2014). With a more complex nonlinear kinetic term along with the partial derivatives in two different directions as will be shown in the following sections will make analytical solution tedious to solve (Chapra & Canale, 2015; Wade, 1999). The numerical approximation has been proven to provide an acceptable solution for the PDEs developed for the equations described in this work (Froment et al., 2011; He, 2003).

The pseudo-homogenous model consists of a single set of equations, assuming the reactor to be a single phase. Equations for the pseudo-homogeneous model as given by Afabor (2015) are as follows:

**Mass Balance:**

\[
D_{er,f} \left( \frac{\partial^2 C_i}{\partial t^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + D_{ez} \frac{\partial^2 C_i}{\partial z^2} - u_z \frac{\partial C_i}{\partial z} + \rho_i v_i r_i = 0
\]  

(3.1)
Energy Balance:

\[
\lambda_{er}\left(\frac{\partial^2 T}{\partial t^2} + \frac{1}{r} \frac{\partial T}{\partial r}\right) + \lambda_{ez} \frac{\partial^2 T}{\partial z^2} - C_{p,f} \rho_f u_z \frac{\partial T}{\partial z} + (-\Delta H_r) \rho_b v_i r_i = 0
\] (3.2)

The heterogeneous model differs from the pseudo-homogeneous model in that it requires another set of governing equations as will be shown in the next section.

### 3.3.1 THE CONVENTIONAL HETEROGENEOUS MODEL

#### 3.3.1.1 BULK FLUID PHASE EQUATIONS

For the bulk fluid phase, the set of equations can be given as follows (Froment et al., 2011; He, 2003):

Mass Balance:

\[
D_{er,f} \left(\frac{\partial^2 C_{i,f}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,f}}{\partial r}\right) + D_{ez,f} \frac{\partial^2 C_{i,f}}{\partial z^2} - u_z \frac{\partial C_{i,f}}{\partial z} + k_{fs}a_v(C_{i,s} - C_{i,f}) = 0
\] (3.3)

Energy Balance:

\[
\lambda_{er,f}\left(\frac{\partial^2 T_f}{\partial t^2} + \frac{1}{r} \frac{\partial T_f}{\partial r}\right) + \lambda_{ez,f} \frac{\partial^2 T_f}{\partial z^2} - C_{p,f} \rho_f u_z \frac{\partial T}{\partial z} + h_{fs}a_v(T_s - T_f) = 0
\] (3.4)

The bulk fluid equations (3.3) and (3.4) can be described as diffusion-convection-reaction equations, with the first three terms representing diffusion and the fourth term is the convection term. The last term on the right-hand side of the equations represents the reaction term, more specifically the mass and heat transfer between the bulk fluid and the
surface of the catalyst. Under steady state conditions, it assumed that reactant consumption is equal to the rate at which they are transferred to catalyst surface (Hill et al, 2014).

### 3.3.1.2 SOLID CATALYST PHASE EQUATIONS

For the solid, spherical catalyst phase, the set of equations can be given as follows (Froment et al., 2011a; He, 2003):

Mass Balance:

\[
\frac{1}{r_s^2}D_{ei} \frac{d}{dr_s} \left( r_s^2 \frac{dC_{i,s}}{dr_s^2} \right) + \rho_s v_i \varepsilon_s (1-\varepsilon_s) = 0
\]  

Energy Balance:

\[
\frac{1}{r_s^2} \lambda_{es} \frac{d}{dr_s} \left( r_s^2 \frac{dT_{i,s}}{dr_s^2} \right) + \rho_s v_i (-\Delta H_r) (1-\varepsilon_s) = 0
\]

The Initial and Boundary conditions applied to these equations given the modelling domain are given as:

1. \( z = 0, 0 \leq r \leq R \):
   \( C_{i,f} = C_{0i} \); \( C_{i,s} = C_{0i} \)  
   \( T_f = T_0 \); \( T_s = T_0 \)

2. \( z = L, 0 \leq r \leq R \):
   \( \frac{\partial C_{i,f}}{\partial z} = 0 \); \( \frac{\partial C_{i,s}}{\partial z} = 0 \)
\[ \frac{\partial T_f}{\partial z} = 0; \quad \frac{\partial T_s}{\partial z} = 0 \quad (3.10) \]

(3) \[ z \geq 0, \quad r = 0 : \]

\[ \frac{\partial C_{i,f}}{\partial r} = 0; \quad \frac{\partial C_{i,s}}{\partial r} = 0 \quad (3.11) \]

(Centerline)

\[ \frac{\partial T_f}{\partial r} = 0; \quad \frac{\partial T_s}{\partial r} = 0 \quad (3.12) \]

(4) \[ z \geq 0; \quad r = r_1 \]

(Wall)

\[ \frac{\partial C_{i,f}}{\partial r} = 0; \quad \frac{\partial C_{i,s}}{\partial r} = 0 \quad (3.13) \]

\[ -\lambda_{er} \frac{\partial T_f}{\partial r} = U_{tw}(T_w - T_f) \quad (3.14) \]

\[ T_s = T_f \quad (3.15) \]

(5) \[ r = R_p: \]

(Pellet Surface)

\[ D \text{im} \frac{dC_{i,s}}{dr} = k_{fs} (C_{i,f} - C_s) \quad (3.16) \]

\[ r = 0 : \]

(Pellet Center)

\[ \frac{dC_{i,s}}{dr} = 0 \quad (3.17) \]

\[ \frac{dT_s}{dr} = 0 \quad (3.18) \]

For these sets of the equations, the parameters can be defined as follows: \( C_{i,f} \) is bulk fluid concentration of species \( i \), mol/m\(^3\); \( C_{i,s} \) is the solid catalyst concentration \( i \), mol/m\(^3\); \( T_f \) is the bulk fluid temperature, K; \( T_s \) is the solid catalyst temperature, K; \( \varepsilon_b \) and \( \varepsilon_a \) is the porosity of the catalyst bed and solid catalyst pellet respectively; \( D_{er,f} \) and \( D_{ez,f} \) is the effective axial and radial diffusivity respectively, m\(^2\)/s; \( D_a \) is the effective diffusivity in the solid phase, m/s. \( \lambda_{er,f} \) and \( \lambda_{ez,f} \) is the effective axial and radial conductivity in the gas phase respectively, J/s-m-K; \( \lambda_{es} \) is the thermal conductivity of the solids phase; \( a_r \) is the particle surface area to volume ratio, m\(^2\)/m\(^3\); \( k_{fs} \) is the effective mass transfer coefficient between solid and gas,
m/s; $h_{fs}$ is the effective heat transfer coefficient between solid and gas, J/s-m²-K; $\rho_f$ and $\rho_s$ is the density of the bulk fluid and solid catalyst respectively; $C_{pf}$ is the heat capacity of the bulk fluid. $z$ and $r$ is the axial and radial direction, m; $u_z$ is the superficial velocity in the axial direction, m/s; $U_{tw}$ is the wall heat transfer coefficient, J/s-m²-K; $v_i$ is the stoichiometric coefficient of component $i$; $r_i$ is the rate of reaction, mol/gcat-s; $\Delta H_{rx}$ is the heat of reaction of the mixture, J/mol.

The subscripts $f$ and $s$ are the indications for fluid and solid properties respectively, $i$ is the indication for a component, while $o$ is for the initial value.

### 3.3.2 SIMULATION ENVIRONMENT FOR THE COVENTIONAL HETEROGENEOUS MODEL

#### 3.3.2.1 COMSOL MULTIPHYSICS

COMSOL Multiphysics is an interactive software with Graphical User Interface (GUI), that employs the Finite Element Method, capable of handling PDEs and DAEs. The software has proven robust enough to apply various physical phenomena to geometries with appropriate boundary conditions and material properties. The relevant equations which the software utilizes to describe the varying phenomena is designed into modules which allows the user to easily enter inputs. The user also has the option of entering their own equations if so desired.

COMSOL Multiphysics has been used in previous research for packed bed reactors, for 1-D and 2-D models of both the pseudo-homogenous and heterogeneous type (Afabor, 2015; Allain & Dixon, 2010; A. G. Dixon, 2012). They have employed various
configurations to achieve their results, such as the Chemical Reaction Engineering Module, Chemical Transport and Heat Transfer Modules.

### 3.3.2.2 COMSOL MULTIPHYSICS MODULE CONFIGURATION

The model development in COMSOL Multiphysics version 5.2A was done over a 2-D rectangular geometry utilizing the Transport of Diluted Species for Mass Transfer module. Newer versions of COMSOL of have a Reactive Pellet sub-module which makes developing the heterogeneous model easier. The user can enter properties for the pellet based on experiments or manufacturer specifications and the software platform generates an extended dimension giving a 1-D radial profile of the pellet.

The Heat Transfer in Fluids module, which is commonly used to generate profiles does not incorporate this feature and assumes that the temperature of the bulk fluid is in equilibrium with the pellet. While there are some papers that ignore the temperature gradient within the pellet by assuming the particle is isothermal, profiles have been generated which account for this effect. Allain (2011) simulated a 2-D heterogenous model utilizing the General Extrusion coupling feature, generating temperature profiles for a pellet. An easier of way of generating temperature profiles was by utilizing the Transport of Diluted Species design for mass transfer for the heat transfer problem. Despite being designed with for mass transfer, with modules tailored towards concentration, equations for heat and mass continuity are of the same form. The general coefficient form for a PDE in COMSOL Multiphysics is expressed as

(ConfTokyo2014Mini_PDE.pdf, 2014):
By having a steady state model with the terms $a$, $e_a$, $\gamma$ and $a$ equal to zero, Equation (3.19) will be of the form given in the Transport of Diluted Species and Heat Transfer model, given as (comsol.com):

$$e \frac{\partial^2 u}{\partial t^2} + d_a \frac{\partial u}{\partial t} - \nabla \cdot (c \nabla u + a u - \gamma) + \beta \cdot \nabla u + a u = f$$

(3.19)

$\nabla$ is the gradient function, and the term $f$ can be represented by $R$, the reaction rate expression (mol/m$^3$·s) or $Q$, the heat source (W/m$^3$). The coefficient term $\beta$ can be replaced with the convection terms $u$ and $\rho C_p u$ for mass and energy respectively which represent the velocity field propagated by heat and mass. The coefficient term $c$ can be replaced with $D$, the diffusion coefficient and $k$ is the thermal conductivity.

There are different approaches for developing the desired solution in this software platform, therefore, as the building block of each model is the same, we can move ahead with our approach for generating temperature profiles within the pellet. This was also validated with data from literature as shown in Appendix F.

Figure 3-2 displays the simulation framework for the CHM. It has three main sections: input, calculations done by the COMSOL solver and the output. The main operating parameters are the input temperature, pressure, pellet size and mole ratios of the feed components. The input parameters are used to determine various physical property calculations such as the heat of reaction, effective diffusivities and effective conductivities and porosity based on the relevant correlations.
Figure 3-2 Conceptual Simulation Framework for executing the CHM in COMSOL Multiphysics
3.3.3 THE ALTERNATIVE HETEROGENEOUS MODEL

The Alternative Heterogeneous model (AHM) will differ from CHM by incorporation of the effectiveness factor $\eta$, defined by Equation (2.9). The CHM model couples the heat and mass transfer between the catalyst pellet and bulk fluid with boundary conditions, while for the AHM, coupling occurs at the surface of the catalyst.

3.3.3.1 BULK FLUID PHASE EQUATIONS

For the bulk fluid phase, the set of equations can be given as follows:

Mass Balance:

$$D_{er,f} \left( \frac{\partial^2 C_{i,f}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,f}}{\partial r} \right) + D_{ez,f} \frac{\partial^2 C_{i,f}}{\partial z^2} - u_z \frac{\partial C_{i,f}}{\partial z} + k_{fs} a_v (C_{i,s} - C_{i,f}) = 0 \quad (3.22)$$

Energy Balance:

$$\lambda_{er,f} \left( \frac{\partial^2 T_f}{\partial r^2} + \frac{1}{r} \frac{\partial T_f}{\partial r} \right) + \lambda_{ez,f} \frac{\partial^2 T_f}{\partial z^2} - C_{p,f} \rho_f u_z \frac{\partial T}{\partial z} + h_{fs} a_v (T_s - T_f) = 0 \quad (3.23)$$

3.3.3.2 SOLID INTERFACIAL PHASE EQUATIONS

At the face of catalyst particle, the set of equations can be given as follows:

Mass Balance:

$$k_{fs} a_v (C_{i,f} - C_{i,s}) + \rho_s v_i r_i \eta (1 - \varepsilon_s) = 0 \quad (3.24)$$
Energy Balance:

\[ h_isa_s(T_f-T_s) + \rho_s v_r T_s \eta (-\Delta H_r) (1-\epsilon_s) = 0 \]  

(3.25)

The boundary conditions that correspond to equations (3.22) and (3.23) will be the same as Equations (3.7) to (3.18) used in the CHM.

3.3.3.3 SOLID INTRA-PELLET PHASE EQUATIONS

For this model, we consider that the pellet, which is a spherical geometry will be subjected to non-isothermal conditions. The temperature and concentration profiles within the pellet allows us to understand any resistances to the reaction rate inside the particle with regards to heat and mass. Equations (3.5) and (3.6) will be utilized to determine the temperature and concentration gradients in the catalyst particle. The boundary conditions that will be used in this case will be slightly differently as the concentration and temperature at the surface of the catalyst can be estimated by solving equations (3.22) to (3.25). The boundary equations for the catalyst pellet will be:

\((1) \quad r = R_p:\)
\[ C_{i,s}(r)= C_{i,s} \]  
\[ r = 0 : \quad \frac{dC_{i,s}}{dr}=0 \]

(Pellet Surface)

\[ T_s(r)= T_s \]  

(Pellet Center)
\[
\frac{dT_s}{dr} = 0
\] (3.29)

The value of \( \eta \) for a catalyst particle located at any position within the reactor can be obtained by integration of the reaction rate from the center of the pellet to the surface calculated the formula:

\[
\eta = \frac{\int_0^{R_p} 4\pi r_p^2 r_i \, dr_p}{\frac{4}{3} \pi r_{i, surface} r_p^3}
\] (3.30)

### 3.3.4 SIMULATION ENVIRONMENT FOR THE ALTERNATIVE HETEROGENEOUS MODEL

The AHM model was developed in MATLAB incorporating solvers designed for handling a system of nonlinear equations and stiff differential equations. MATLAB boasts as a robust software platform which can generate workspaces for troubleshooting as well as interfaces that generate graphical displays.
Figure 3-3 Conceptual Simulation Framework for executing the AHM in MATLAB
3.3.4.1 NON-DIMENSIONALIZATION

A common practice in modelling physical phenomena is converting the model equations to a dimensionless form. The main advantages of the reduction in code complexity and an increase in computational efficiency when generating a solution. Despite the introduction of modern computers with faster, more powerful processors, as well as software packages which have built-in codes to handle problems that may challenge numerical stability such as stiffness, converting an equation to a dimensionless form allows is still a worthwhile practice.

For this work, we can define the following dimensionless groups (Nauman, 2008; Wade, 1999):

\[ \bar{z} = \frac{z}{L} \]
\[ \bar{\tau} = \frac{r}{R} \]
\[ \text{Pe}_{zm} = \frac{d\bar{p}}{u_z} \frac{D_e z}{D_e z} \]
\[ \text{Pe}_{rm} = \frac{d\bar{p}}{u_r} \frac{D_e r}{D_e r} \]
\[ \bar{C}_i = \frac{C_i}{C_{i,0}} \]
\[ \bar{T} = \frac{T}{T_o} \]
\[ \text{Pe}_{zh} = \frac{d\bar{p} u_z \rho_f C_{p,f}}{\lambda_c z} \]
\[ \text{Pe}_{rh} = \frac{d\bar{p} u_z \rho_f C_{p,f}}{\lambda_{er}} \]
\[ \bar{\alpha} = \frac{L d\bar{p}}{R^2} \]
\[ \bar{\delta} = \frac{L}{d\bar{p}} \]
\[ \text{Bi} = \frac{U_{tw} R}{\lambda_{er}} \]
\[ \text{Damk} = \frac{r_i L}{u_z} \]
\[ \beta = \frac{-\Delta H_{rx} C_1}{\rho_f T_0 C_{p,f}} \]
\[ \text{Stm} = \frac{k_{fs} a_v L}{u_z} \]
\[ \text{Sth} = \frac{h_{fs} a_v L}{\rho_f C_p u_z} \]

For engineering purposes, making the system of equations dimensionless essentially scales them to a common factor, where the impact of each term in the model can be assessed easier. This technique has proved useful in also reducing the computational load when running the solver (Nauman, 2008). Although not the focus of this thesis,
researchers have developed relationships between Fluid Peclet (Pe) numbers and Reynolds Number to draw better conclusions on fluid dynamics within the reactor.

Programming techniques by Beers (2006) and Finlayson (2012) were used to solve the AHM equations after being discretized for each component of the reaction. The 2-D domain equations were solved using the ode15s solver.

The solver increments the system of differential equations over the axial span of the domain. The PDEs to describe the bulk fluid equations are discretized using a central finite difference approximation, which is a common approach used in literature.

Using these dimensionless terms, equations (3.22) to (3.25) can be rewritten as:

**Mass Balance:**

\[
\frac{\partial C_f}{\partial Z} = \frac{\alpha}{P_{erm}} \left( \frac{\partial^2 C_f}{\partial Z^2} + \frac{1}{r} \frac{\partial C_f}{\partial r} \right) + \frac{1}{P_{ezm}} \frac{\partial^2 C_f}{\partial Z^2} + Stm \left( C_s - C_f \right)
\]  

(3.31)

**Energy Balance:**

\[
\frac{\partial T}{\partial Z} = \frac{\alpha}{P_{erh}} \left( \frac{\partial^2 T_f}{\partial Z^2} + \frac{1}{r} \frac{\partial T_f}{\partial r} \right) + \frac{1}{P_{ezh}} \frac{\partial^2 T_f}{\partial Z^2} + Sth \left( T_s - T_f \right)
\]  

(3.32)

**Mass Balance(Inter-facial):**

\[
Stm \left( C_{i,f} - C_{i,s} \right) + \text{Damk} v_i \bar{r}_i \eta(1-\epsilon_b) = 0
\]  

(3.33)

**Energy Balance(Inter-facial):**

\[
Sth \left( T_f - T_s \right) + \text{Damk} v_i \bar{r}_i \eta(1-\epsilon_b) = 0
\]  

(3.34)
The solver functions to handle differential equations from the order of 1 to 5, and with the presence of the second order, axial dispersion term, a dummy variable \( w \), which requires equations (3.31) and (3.32) are rearranged as:

\[
\frac{\partial \bar{C}}{\partial \bar{z}} = w \tag{3.35}
\]

\[
\frac{\partial \bar{w}}{\partial \bar{z}} = \text{Pe}_{zm} \left( w - \frac{\alpha}{\text{Pe}_{zm}} \frac{\partial^2 \bar{C}_f}{\partial \bar{T}_f^2} + \frac{1}{\bar{r}} \frac{\partial \bar{C}_f}{\partial \bar{T}_f} \right) - \text{Stm} \left( \bar{C}_s - \bar{C}_f \right) \tag{3.36}
\]

\[
\frac{\partial \bar{T}}{\partial \bar{z}} = w \tag{3.37}
\]

\[
\frac{\partial \bar{w}}{\partial \bar{z}} = \text{Pe}_{zh} \left( w - \frac{\alpha}{\text{Pe}_{zh}} \frac{\partial^2 \bar{T}_f}{\partial \bar{T}_f^2} + \frac{1}{\bar{r}} \frac{\partial \bar{T}_f}{\partial \bar{T}_f} \right) - \text{Sth} \left( \bar{T}_s - \bar{T}_f \right) \tag{3.38}
\]

This technique was utilized by Wade, (1999), using a custom code developed in FORTRAN. This rearrangement of the equations will allow the PDEs to be written in a form that is acceptable to the solver.

For the intra-pellet phase, a spherical catalyst was used, equations (3.5) can be written in a non-dimensional form as follows:

\[
\frac{1}{\bar{r}_s} \frac{d}{d \bar{r}_s} \left( \bar{r}_s^2 \frac{d \bar{C}_{1,s}}{d \bar{r}_s^2} \right) + v_1 \phi^2 \exp \left( \frac{\gamma \beta \left( 1 - \bar{C}_1 \right)}{1 + \beta \left( 1 - \bar{C}_1 \right)} \right) \bar{C}_1 \bar{C}_2 \bar{C}_3 = 0 \tag{3.39}
\]

The three important dimensionless parameters \( \phi, \beta \) and \( \gamma \) can be calculated as:
\[ \phi = r_p \sqrt{\frac{R(C,T)}{C_{1s} D_{es,1}}} \]

\[ \beta = \frac{D_{es,1}(-\Delta H_{rx})C_{1s}}{\lambda_s T_s} \]

\[ \gamma = \frac{E_a}{R_g T_s} \] (3.40)

With a non-isothermal catalyst, the temperature inside the reactor can be related to the concentration of component \( C_1 \) with the relationship:

\[ T(r) = T_s + \frac{D_{es,1}(-\Delta H_{rx})}{\lambda_s} (C_1(r)-C_{1s}) \] (3.41)

The rate of reaction \( r_i \) (C, T), is dependent upon the concentration of synthetic crude glycerol, steam and oxygen which are represented in Equation (3.39) as \( C_1 \), \( C_2 \) and \( C_3 \) respectively. Previous experimental work done has indicated that the diffusivity within the catalyst particle does not demonstrate significant changes along the pores, which allows us to establish dependent relationships between the concentration of the main component of crude glycerol and other components as follows (Kim et al, 2004, Lee et al, 2004):

\[ C_i - C_{is} = \frac{v_i D_{es,1}}{D_{es,i}} (C_1 - C_{1s}) \] (3.42)

In the linear relationships given in (3.41) and (3.42) the subscript ‘s’ denotes the condition at the surface of the catalyst where the effective diffusivity along the axial length of the at the surface of the catalyst must be determined using the Stefan-Maxwell correlations.

The boundary conditions for the new dimensionless equations are written as:

(1) \( z = 0, 0 \leq r \leq R \):

\[ \bar{C}_{1i} = \bar{C}_{0i} ; \bar{C}_{i,s} = \bar{C}_{0i} \] (3.43)

(Inlet)
\( T = T_0; \bar{T}_s = \bar{T}_{0i} \) \hfill (3.44)

(2) \( z = L, 0 \leq r \leq R \):

\( \frac{\partial \bar{C}_{i,f}}{\partial z} = 0; \frac{\partial \bar{C}_{i,s}}{\partial z} = 0 \) \hfill (3.45)

(Outlet)

\( \frac{\partial \bar{T}_f}{\partial z} = 0; \frac{\partial \bar{T}_s}{\partial z} = 0 \) \hfill (3.46)

(3) \( z \geq 0, r = 0 \):

\( \frac{\partial \bar{C}_{i,f}}{\partial r} = 0; \frac{\partial \bar{C}_{i,s}}{\partial r} = 0 \) \hfill (3.47)

(Centerline)

\( \frac{\partial \bar{T}_f}{\partial r} = 0; \frac{\partial \bar{T}_s}{\partial r} = 0 \) \hfill (3.48)

(4) \( z \geq 0; r = r_1 \)

\( \frac{\partial \bar{C}_{i,f}}{\partial r} = 0; \frac{\partial \bar{C}_{i,s}}{\partial r} = 0 \) \hfill (3.49)

(Wall)

\( \frac{\partial \bar{T}_f}{\partial r} = -\text{Bi}(\bar{T}_w - \bar{T}_f) \) \hfill (3.50)

\( \bar{T}_w = \bar{T}_s \) \hfill (3.51)

(5) \( r = R_p \):

\( \bar{C}_{i,s}(r) = \bar{C}_{i,s} \) \hfill (3.52)

(Pellet Surface)

\( \bar{T}_{i,s}(r) = T_{i,s} \) \hfill (3.53)

(6) \( r = 0 \):

\( \frac{d\bar{C}_{i,s}}{dr} = 0 \) \hfill (3.54)

(Pellet Center)

\( \frac{d\bar{T}_s}{dr} = 0 \) \hfill (3.55)
The MATLAB solver \textit{fsolve} was used to solve the Equation (3.39). This solver is
designed to handle nonlinear system of equations with specified by the function \( F(x) = 0 \).

\subsection*{3.3.4.2 DISCRETIZATION IN MATLAB}

The computational domain for the model development is shown in Figure 3-4.
Figure 3-4 Simple discretization of 2-D Domain
In the radial direction, the domain with a length R, is divided into the equal spacing of grid points by the formula $\Delta r = \frac{R}{N}$, where N is the maximum number of grid points in the r-direction.

Generically, the discretization of the PDEs given as those in equations (3.35) to (3.38), if written generically can be given as:

$$\frac{\partial u}{\partial z} = w_{f,i}$$ (3.56)

$$\frac{\partial w_{f,j}}{\partial z} = P_e \left( w_{f,j} - \frac{\alpha}{P_e} \left( \frac{u_{f,j+1} - 2u_{f,j} + u_{f,j-1}}{\Delta r^2} + \frac{1}{r_j} \frac{u_{f,j+1} - u_{f,j-1}}{2\Delta r} \right) - St \left( u_{sj} - u_{\xi j} \right) \right)$$ (3.57)

$$St \left( u_{rj} - u_{sij} \right) + r_i = 0$$ (3.58)

In this generic form, the ODE solvers provided by MATLAB can be utilized to generate the desired solution. The solver suite utilizes numerical differentiation formulas, incrementing in the axial direction under to generate a profile across the entire 2-D domain (Shampine & Reichelt, 1997). The radial profiles generated by the solver are averaged with Simpson’s rule to generate bulk fluid temperature and concentration profiles. At each position along the reactor length, the spherical pellet equations are solved, where the effectiveness factor given in equation (3.30) is calculated using the trapezoid rule. The equations for the pellet were discretized on a 1-D domain as shown in Figure 3-5.
Figure 3-5 Discretization of grid points for 1-D domain
The generic discretization for these nodes is given as:

\[
\frac{(u_{s,j+1} - 2u_{s,j} + u_{s,j-1})}{\Delta r^2} + \frac{2}{r} \left( \frac{u_{s,j+1} - u_{s,j-1}}{2\Delta r} \right) = r_j
\]

(3.59)

A central difference discretization is done again for solving profiles in the pellet domain. A minimum number of grid points is needed to give a good approximation of the profiles required for this model.

Figure 3-6 gives shows the effect of changing the grid points on the approximation solution. From a qualitative standpoint, the profile becomes smoother and the approximations become closer as the number of grid points increases. The dimensionless radius is based on a spherical pellet of radius 0.4 mm and with the number of grid points greater than 61, there is no significant difference in the approximation. Above 61 grid points, it is shown that there is no difference in the approximation.
Figure 3-6 Relationship between number of grid points and approximation of crude glycerol approximation
3.3.5 KINETIC RATE MODEL

The reaction rate $r_i$ for this work was referenced from previous experiments performed by Abdul Ghani (2014), where a power law model was developed given as:

$$r_{C_{2.5}H_{7}O_{2}} = 2.09 \times 10^{11} \ e^{-\frac{93700}{RT}} \ p_{C_{2.5}H_{7}O_{2}}^{p_{H_{2}O}}^{0.5} \ p_{O_{2}}^{2}$$  \hspace{1cm} (3.60)$$

The reaction for the ATR of synthetic crude glycerol was given as:

$$C_{2.5}H_{7}O_{2} + a H_{2}O + bO_{2} \rightarrow 0.5 \ CH_{4} + 2 \ CO_{2} + c H_{2} + d H_{2}O$$  \hspace{1cm} (3.61)$$

reaction based on the different components used to make up the synthetic crude oil. The coefficients for $a$, $b$, $c$ and $d$ and initial conditions for this work were given from previous experiments performed in Tables 4.6 and 4.8 from Abdul Ghani (2014). The reaction term used for this work is nonlinear which adds complication to solution convergence issues when applying the relevant numerical methods. With algorithms such as \textit{fsolve}, the Jacobian can be user-supplied or it can be approximated by the solver (Beers, 2006). In some cases, the user-supplied Jacobian reduces the execution time of the solution, but this was not required for this work.

3.4 SUPPORT EQUATIONS

For this work, calculations for physical properties will be required for the following:

- Heat of Reaction
- Pressure Drop
Density

Effective Transport Properties

3.4.1 HEAT OF REACTION

The Heat of Reaction, $\Delta H_{rx}$ of the feed mixture is determined by the following calculation:

$$\Delta H_{rx} = H_i^0 + \Delta H_{Qi} \quad (3.62)$$

Where $H_i^0$ is the Heat of formation of a species $i$ and $\Delta H_{Qi}$ represents the enthalpy change from a reference temperature in kJ/mol. The reference temperature is expressed in textbooks at 25°C (Fogler, 2011). When there is no phase change $\Delta H_{Qi}$ is calculated by:

$$H_{Qi} = \int_{T_1}^{T_2} C_{pi}dT \quad (3.63)$$

The heat capacity $C_{pi}$ is determined by polynomial expressions (Perry, Green, & Maloney, 1997):

$$C_{pi} = A + BT + CT^2 + DT^3 + ET^4 \quad (3.64)$$

3.4.2 PRESSURE DROP

The pressure drop in the reactor is of importance when managing industrial reactors. The pressure drop can be determined by the Ergun equation, which for a fixed bed can be given as (Fogler, 2011):
\[ \frac{\partial P}{\partial Z} = 150 \mu u_z \frac{(1-\epsilon_b)^2}{\epsilon_b^2} + \frac{1.75 \rho_b u_z^2}{d_p} \frac{(1-\epsilon_b)^2}{\epsilon_b^2} \] (3.65)

### 3.4.3 DENSITY

The ATR of glycerol is performed at the 773-923K and under atmospheric pressure. At high temperatures and low pressure, the feed mixture will assume to behave as an ideal gas (Scognamiglio, 2008). The density of the mixture can be calculated as:

\[ \rho_f = \frac{P \ M_{avg}}{R_g \ T_f} \] (3.66)

where \(M_{avg}\) is average molecular weight of the feed mixture, kg/mol; \(R_g\) is the Ideal Gas Constant, J/mol/K.

### 3.4.4 EFFECTIVE DIFFUSIVITY

For Effective Radial and Axial Diffusivity, the following correlations can be used (He, 2003; Iordanidi, 2002):

\[ D_{er} = \frac{u_z d_p}{\left(7 \times \left(1 + 19.4 \left(\frac{d_p}{D_p}\right)^2\right)\right)^{0.5}} \] (3.67)

\[ D_{ez} = Q d_p \left(0.5 + \frac{0.38}{N_{RE}}\right) \] (3.68)
Q is the volumetric flowrate into the reactor, m$^3$/s. $N_{RE}$ is the Reynolds number given by:

$$N_{RE} = \frac{\rho_f u_x d_p}{\mu(1-\varepsilon_b)} \quad (3.69)$$

Diffusion into the catalyst is governed by different phenomena than the diffusivity of the bulk fluid in a heterogeneous system. Equimolar counter-diffusion takes place in the catalyst dependent upon the pore geometry. The Effectivity Diffusivity for the solid catalyst, $D_{es,i}$ is described by the following equation (Fogler, 2011):

$$D_{es,i} = \frac{D_{AB} \varepsilon_s}{\tau} \quad (3.70)$$

Where $D_{AB}$ is the ordinary bulk diffusivity in a binary gaseous mixture, m$^2$/s, $\tau$ is tortuosity path of the particle. The Fuller-Schettler- Giddings correlation given in Equation (3.69) (Hill & Root, 2014):

$$D_{AB} = 10^{-3} T^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5} \frac{P}{\left[ (\sum V_A)^{1/3} + (\sum V_B)^{1/3} \right]^2} \quad (3.71)$$

With the Binary Diffusivity between the two species in a particle, the Diffusivity of a species within a mixture is given as (Hill & Root, 2014):

$$D_{im} = \frac{1 - y_i}{\sum_j \frac{N_j}{N_i} \frac{y_j}{y_i}} \frac{y_j}{y_i} \frac{N_j}{N_i} D_{ij} \quad (3.72)$$

$M$ is the Molecular weight of the component, g/mol; $V$ is the diffusion volume; $N$ is the molar flux mol/s.
3.5 EXPERIMENTATION

3.5.1 ATR EXPERIMENTS

The physical experiments for the ATR process being modelled in this work were done under the portfolio of the Advanced Green Energy Systems Research Group at the University of Regina by Abdul Ghani (2014). Batches of a synthetic crude glycerol composed of various chemicals with the composition given in Appendix A. As given by equation (3.57), the main reactants along with the synthetic crude glycerol were steam and oxygen. The schematic is shown in Figure 3-7. Based on the required steam to carbon ratio, water was mixed into the batch of the synthetic crude glycerol. Simultaneously, based on the oxygen to carbon ratio, air was fed into the laboratory scale reactor, with a catalyst bed being 45 mm in length and 12.7 mm in diameter, in the ratio of approximately 21% oxygen and 79% nitrogen. After the reactants were passed through the cylindrical reactor packed with spherical catalyst pellets, where the outlet gas was passed through a condenser, removing the water, where the remaining gas was analyzed with a gas chromatograph (GC). Parametric studies were performed in their work to results used to establish kinetics were performed under varying conditions temperature and pressure and catalyst weights varying from 0.05 to 0.25g, under conditions which would not inhibit and effective contribution of the catalyst to the reaction.
Figure 3-7 Experimental setup for ATR process experiments (Abdul Ghani, 2014)
3.5.1 PRESSURE DROP DATA

For an industrial reactor operation, the pressure drop in the reactor is an important parameter because it affects the operating costs when it comes to pumping and compression (Ghouse & Adams, 2013; MacDonald, 2014). The laboratory setup at the University of Regina used for the ATR process did not account for the pressure drop, though it may be insignificant for a tube with small dimensions. The Ergun equation given in equation (3.66) is a commonly used correlation in literature to estimate the pressure drop in the reactor. Therefore, to translate the equation to this work, experimental data from Pešić et al. (2015) was used to validate the equation.

Figure 3-8 gives a schematic of the experimental setup used by (Pešić et al., 2015). They used a Plexiglass cylindrical column packed with spherical glass beads with different diameters. Different experimental runs were performed at a controlled temperature and varying bed voidages as the pressure of hot air flowing through the bed was measured. Equation (3.66) can be rewritten as:

\[ f_p = \left( \frac{\partial P}{\partial Z} \right) \frac{d_p}{\rho_f u_z} \frac{\varepsilon^3}{1-\varepsilon} \]  

(3.73)

Where \( f_p \) is the friction factor and for Ergun can be given as follows

\[ f_p = \frac{150}{\left( \rho_f u \frac{d_p}{\mu} \right)} + 1.75 \]  

(3.74)

In their work, they compared fifteen correlations published for the friction factor and concluded Ergun provided the best fit for their data. The results they plotted are given in Appendix E.
Figure 3-8 Experimental setup for pressure drop experiments used by (Pešić et al., 2015)
CHAPTER 4: RESULTS AND DISCUSSION

4.1 PREDICTIVE PERFORMANCE OF NUMERICAL MODEL

The input values for the model are given in the following table:

Table 4-1 Input Parameters for Initial Run for Laboratory Simulation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Definition and units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{er}^*$</td>
<td>Effective Gas Radial Conductivity, W/m-K</td>
<td>0.063</td>
</tr>
<tr>
<td>$\lambda_{ez}^*$</td>
<td>Effective Gas Axial Conductivity, W/m-K</td>
<td>0.063</td>
</tr>
<tr>
<td>$\lambda_{es}^{**}$</td>
<td>Catalyst Conductivity, W/m-K</td>
<td>0.348</td>
</tr>
<tr>
<td>$a_v$</td>
<td>Particle surface area to volume ratio, m$^2$/m$^3$</td>
<td>4476.2</td>
</tr>
<tr>
<td>$C_p^*$</td>
<td>Heat capacity, J/kg-K</td>
<td>1920</td>
</tr>
<tr>
<td>D</td>
<td>Internal reactor diameter, mm</td>
<td>12.7</td>
</tr>
<tr>
<td>$D_{er}$</td>
<td>Effective Gas Radial Diffusivity, m$^2$/s</td>
<td>$5.55 \times 10^{-5}$</td>
</tr>
<tr>
<td>$D_{ez}$</td>
<td>Effective Gas Axial Diffusivity, m$^2$/s</td>
<td>$7.37 \times 10^{-5}$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Catalyst particle diameter, mm</td>
<td>0.8</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation energy, J/mol</td>
<td>93700</td>
</tr>
<tr>
<td>$F_{CG0}$</td>
<td>Inlet Molar Flowrate of Crude Glycerol, mol/s</td>
<td>$1.3067 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Frequency Factor, mol C kgcat$^{-1}$ min$^{-1}$ atm$^{-3.5}$</td>
<td>$2.09 \times 10^{11}$</td>
</tr>
<tr>
<td>L</td>
<td>Packed bed length, mm</td>
<td>45</td>
</tr>
<tr>
<td>$M_{ave}$</td>
<td>Average molecular weight of Reactor Feed Mixture, g/mol</td>
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</tr>
<tr>
<td>$P_{tot}$</td>
<td>Total pressure, atm</td>
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<td>$T_0$</td>
<td>Inlet temperature, K</td>
<td>773</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Environment temperature, K</td>
<td>773</td>
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<tr>
<td>$U_{tw}^*$</td>
<td>Heat transfer coefficient, W/m$^2$ °C</td>
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</tr>
<tr>
<td>$W/F_{A0}$</td>
<td>Space time, g cat min/mol C</td>
<td>12.71</td>
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<tr>
<td>$y_{CG0}$</td>
<td>Inlet crude glycerol mole fraction</td>
<td>0.1</td>
</tr>
<tr>
<td>$y_{N20}$</td>
<td>Inlet nitrogen mole fraction</td>
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</tr>
<tr>
<td>$y_{O20}$</td>
<td>Inlet oxygen mole fraction</td>
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</tr>
<tr>
<td>$y_{steam0}$</td>
<td>Inlet steam mole fraction</td>
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<td>$\varepsilon_b$</td>
<td>Catalyst bed porosity</td>
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<tr>
<td>$\varepsilon_x$</td>
<td>Catalyst Pellet porosity</td>
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<tr>
<td>$\mu^*$</td>
<td>Viscosity, Pa s</td>
<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Gas Density, kg/m$^3$</td>
<td>0.388</td>
</tr>
</tbody>
</table>

*-Values referenced from (Afabor, 2015)

** Values referenced from (Ghouse & Adams, 2013)
The output conversions obtained from Abdul Ghani, (2014) were compared with the predicted output conversion of synthetic crude glycerol using the heterogeneous model developed by both with FEM and FDM. The conversion in the reactor was determined by the following formula:

\[
\text{Conversion(\%)} = \frac{C_{CG \text{ into reactor}} - C_{CG \text{ at reactor outlet}}}{C_{CG \text{ into reactor}}} \times 100
\]  

(4.1)

The parity plot given in Figure 4-1 shows the conversions obtained for a temperature range of 773-923K for a W/F_{A0} of 12.71-158.23 g cat min/mol C.
Figure 4-1 Comparison of measured and predicted crude glycerol conversion for temperature and space time ranges of 773 K - 923 K and W/FA0 of 12.71 - 158.23 g cat min/mol C respectively
Figure 4-1 gives us the AAD of the heterogeneous models done by FEM and FDM, where were 7.56% and 6.34% respectively, which can give an initial indication of the validity of the numerical models. The simulation data used in the parity plot is given in Table 4-2. The experimental conversions were obtained from the experiments performed from Abdul Ghani (2014). The mole fraction of components as given by the GC analysis were compared against the mole fractions given by the numerical model. An example of two runs were given in the tables 4-3 and 4-4 below.
### Table 4-2 Experimental and Prediction Conversion Results

<table>
<thead>
<tr>
<th>Run #</th>
<th>Feed Temperature (K)</th>
<th>W/FA0 (g cat min/mol C)</th>
<th>Experimental (%) (Abdul Ghani, 2014)</th>
<th>FEM Simulation (%)</th>
<th>AAD (%)</th>
<th>FDM Simulation (%)</th>
<th>AAD (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>773</td>
<td>12.71</td>
<td>45.25</td>
<td>36.67</td>
<td>18.96</td>
<td>38.30</td>
<td>15.36</td>
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<td>2</td>
<td>773</td>
<td>50.97</td>
<td>50.15</td>
<td>60.22</td>
<td>20.08</td>
<td>55.71</td>
<td>11.09</td>
</tr>
<tr>
<td>3</td>
<td>773</td>
<td>76.47</td>
<td>55.34</td>
<td>70.97</td>
<td>28.24</td>
<td>66.58</td>
<td>20.31</td>
</tr>
<tr>
<td>4</td>
<td>773</td>
<td>101.94</td>
<td>56.99</td>
<td>76.22</td>
<td>33.74</td>
<td>72.82</td>
<td>27.78</td>
</tr>
<tr>
<td>5</td>
<td>823</td>
<td>12.71</td>
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<td>61.65</td>
<td>10.78</td>
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<td>1.65</td>
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<td>20</td>
<td>873</td>
<td>96.86</td>
<td>92.45</td>
<td>92.53</td>
<td>0.09</td>
<td>90.59</td>
<td>2.01</td>
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<tr>
<td>21</td>
<td>873</td>
<td>127.42</td>
<td>90.54</td>
<td>86.70</td>
<td>4.24</td>
<td>86.67</td>
<td>4.27</td>
</tr>
<tr>
<td>22</td>
<td>873</td>
<td>158.23</td>
<td>86.94</td>
<td>80.17</td>
<td>7.79</td>
<td>72.62</td>
<td>16.47</td>
</tr>
</tbody>
</table>

**AAD** | **7.56** | **6.34**
Table 4-3 Outlet Concentration Profile of the PBTR at a Feed Temperature of 873 K and W/FA0 of 76.47 gcat min/mol C

<table>
<thead>
<tr>
<th>Component</th>
<th>Measured Mole Fraction (%) (Abdul Ghani 2014)</th>
<th>Predicted Mole Fraction (FEM) (%)</th>
<th>Predicted Mole Fraction (FDM) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>39.62</td>
<td>38.71</td>
<td>38.47</td>
</tr>
<tr>
<td>CO₂</td>
<td>22.09</td>
<td>22.59</td>
<td>22.63</td>
</tr>
<tr>
<td>O₂</td>
<td>0.018</td>
<td>0.017</td>
<td>0.0148</td>
</tr>
<tr>
<td>N₂</td>
<td>31.16</td>
<td>33.54</td>
<td>33.46</td>
</tr>
<tr>
<td>CH₄</td>
<td>7.11</td>
<td>5.65</td>
<td>5.66</td>
</tr>
</tbody>
</table>

AAD(FEM) = 7.67%

AAD(FDM) = 10.20%

Table 4-4 Outlet Concentration Profile of the PBTR at a Feed Temperature of 923 K and W/FA0 of 127.42 gcat min/mol C

<table>
<thead>
<tr>
<th>Component</th>
<th>Measured Mole Fraction (%) (Abdul Ghani 2014)</th>
<th>Predicted Mole Fraction (FEM) (%)</th>
<th>Predicted Mole Fraction (FDM) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>40.3</td>
<td>38.84</td>
<td>38.14</td>
</tr>
<tr>
<td>CO₂</td>
<td>21.17</td>
<td>23.29</td>
<td>23.47</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0079</td>
<td>0.008</td>
<td>0.0044</td>
</tr>
<tr>
<td>N₂</td>
<td>30.14</td>
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<td>31.75</td>
</tr>
<tr>
<td>CH₄</td>
<td>8.31</td>
<td>5.82</td>
<td>5.87</td>
</tr>
</tbody>
</table>

AAD(FEM) = 10.84%

AAD(FDM) = 10.20%
Tables 4-3 and 4-4 give two different outputs from the GC at different conditions which gave acceptable AAD with the maximum being 10.84%. Based on the AAD, the FDM provides slightly more accurate conversions.

4.2 COMPARISON OF THE AHM AND CHM MODEL

The system of equations was solved with two different numerical techniques, FDM and FEM, which has been performed in previous studies for various systems not associated with a PBTR.

Figures 4-2 and 4-3 show the temperature and concentration profiles for two heterogeneous models, both developed with the FDM ‘in-house’ code and FEM in COMSOL Multiphysics; as well as a pseudo-homogeneous model developed with the FDM in-house code. The previously built pseudo-homogeneous model was developed by Afabor (2015) for the ATR of synthetic crude glycerol. It should be noted that for this comparison of the four models, the heat of reaction was assumed to be 65.2 kJ/mol used by Afabor (2015) in their model. From the data, the inclusion of governing equations for the solid catalyst shows a reduction in temperature of the reaction zone. The heterogeneous models have a reaction zone temperature approximately 5°C less than that of the pseudo-homogeneous model. It is also observed that the reaction zone is shifted further from the inlet of the reactor for the heterogenous models. Another observation is that for pseudo-homogeneous model developed with the ‘in-house’ code, the gradient after the reaction zone is steeper than that for the FEM model. This can be attributed to the different solvers being used for development, what is important in the scenario is that reaction zone predicted temperatures are in good agreement.
The deviations in Figure 4-3 between the concentration profiles are almost negligible. Similar observations were seen in simulations done by Iordanidi (2002) and Rout et al. (2015), indicating that the reaction may be more sensitive to temperature than to the concentration of the reactants, and that heat and mass transfer rates across the boundary layer of catalyst particles influence the predicted temperature and concentration in the reactor.
Figure 4-2 Bulk Fluid Temperature Profile along length of reactor at 873K and W/FA0 of 12.71 g cat min/mol C
Figure 4-3 Bulk Fluid CG Concentration Profile along length of reactor at 873K and W/FA0 of 12.71 g cat min/mol C

Criterion developed by Mears has been used in previous research to determine the onset of interphase limitations of heat and mass, which allows us to researchers to eliminate the
need for developing a heterogeneous model, as it assumes there will be virtually no difference between the temperature and concentration in solid and fluid phases (Fogler, 2011). This also forms the basis of developing kinetic experiments. For a laboratory scale experiment, the differences between the phases may exists but can be neglected depending on the conditions under which the reactor operates. However, for a comprehensive model, it can prove beneficial to simulate as much phenomena as possible occurring inside the reactor.

By solving the equations for mass and heat transfer within the catalyst pellet. Moreover, to further compare the models developed, we also compared the concentration profiles inside a catalyst particle under two different conditions. R-squared values in this scenario for temperature and concentration were 0.995 and 0.994 respectively.
Figure 4-4 Crude Glycerol Concentration inside pellet at 773K, W/FA0 of 76.47, at 10 mm from the inlet of reactor
Figure 4-5 Temperature inside pellet at 773K, W/FA0 of 76.47, at 10 mm from the inlet of reactor
In the figures presented above comparing the pseudo-homogeneous and heterogeneous models, there is a distinguishable difference in the profiles, especially for predicted temperature in the reactor. Similar profiles are seen in the work done by Iordanidi (2002) and Rout et al. (2015). At steady state, the lower temperatures in the reaction zone are predicted due to the rates of heat and mass transfer at the face of the catalyst being accounted for.

In the figures displayed for this work, the models for the CHM and AHM do not match up with exact precision, however this could be attributed to the two different software platforms which were used to produce the models. The algorithms developed for COMSOL Multiphysics solutions are not open-source and cannot be obtained to replicate. The ODE solver used in MATLAB may not be the same as that used in COMSOL Multiphysics resulting in the deviations. Finlayson (2012) compared different numerical techniques using a single software platform MATLAB for an axial dispersion problem and obtained identical results. A similar approach was also investigated by Roohi et al. (2014), with high R-squared values, however, their approach was done using two numerical methods within the same software platform. Nevertheless, it is shown that for this work the two different models developed can be used for the simulation required. By using the Reactive Pellet module in COMSOL Multiphysics designed for solving concentration and applying it to solve for temperature in the pellet, it was shown to give an acceptable prediction. With the comparison, despite present overlaps in trends, it was important that trending of the properties is occurring in the same manner.
Developing a custom may provide the researcher absolute control over customization of a model. However, the COMSOL Multiphysics interface is a less time-consuming method of developing the model with less effort required to produce a solution as opposed to writing code. An experienced user of COMSOL Multiphysics is also able to integrate the mathematical functions that are used in programming software such as MATLAB, C or FORTRAN, allowing users to increase sophistication of the model if desired. Because of the ease of data collection, the remaining results in this work, apart from the effectiveness factor values will be given using the CHM in COMSOL Multiphysics.

4.3 EFFECT OF AXIAL DISPERSION ON H₂ YIELD

The topic of axial dispersion in both heat and mass transfer has been debated in literature over the past decades with regards to inclusion into models. As the fluid moves through the reactor, there will be temperature and concentration gradients that will be present in both the axial and radial directions. In previous work done by Akande et al. (2006), neglecting the axial terms had notable impact on conversion and fluid temperature, while Afabor (2015) considered the axial terms to be negligible, having no impact on the overall solution. Analogous to criterion for determining plug flow within a PBTR, there have been different criterion proposed for neglecting axial terms, with the simplest being $L/d_p > 30$. Fogler (2011) indicated that axial dispersion may prove important to the model in laboratory experiments with small scale dimensions, while in an industrial setting, with higher flowrates and forced convection, axial dispersion can be neglected.

Figure 4-6 shows the bulk fluid temperature and crude glycerol conversion along the reactor with an inlet temperature of 773K and a space time of 76.47 g cat min/mol C.
Figure 4-6 Bulk Fluid Temperature and Crude Glycerol Conversion along the length of the reactor with a feed temperature of 773K and W/FA0 of 76.47 g cat min/mol C
At this space time of the 76.47 g cat min/mol C, the over-prediction up to 15 cm along the length of the reactor gives a maximum 6°C difference for the temperature profile without axial dispersion, however after the reaction zone is reached, the temperature trends converge. The conversion profile at this space time under-prediction occurs at the front end of the reactor then over-prediction occurs, without axial dispersion. The difference in the final conversion of crude glycerol is negligible.

The feed temperatures were increased from 773 K to 923K, and the differences in the profiles and temperature also gave minute differences in the temperature and conversion. It should be noted however, that for the temperature trends, without axial dispersion, the reaction zone occurs closer to the inlet of the reactor, with the predicted temperature exiting the reactor being 3°C lower than the predicted temperature with axial dispersion.
Figure 4-7 Bulk Fluid Temperature and Crude Glycerol Conversion along the length of the reactor with a feed temperature of 76.47 g cat min/mol C
For this work, there was no significant difference in the models developed with and without the axial dispersion term. Similar observation was made by Afabor (2015). Unlike prior analysis by Akpan (2008) and Akande et al. (2006), which gave under predictions without the use of the axial terms, the models here do not necessarily do follow a similar behavior in all cases. Axial dispersion models by Young et al. (1973) gave over-predictions with temperature and conversion. Under laboratory scale conditions, axial dispersion may tend to become more apparent, unlike industrial scale reactors with higher velocities. The trend in Figure 4-7, with axial dispersion, the temperature is overpredicted until the reaction zone is reached, where after the temperature is lower compared to the trend which is not inclusive of axial dispersion term. The enhanced effect of the second order term along with the endothermic nature that will occur at the components approach the end of the reactor accounts for this.

For a laboratory scale, the simple L/dp ratio for this laboratory scale model is 56.25 is greater than the limit of 30, as well as the limit of 50 given by Froment et al. (2011).

A radial profile was also displayed as shown in Figures 4-8.
Figure 4-8 Radial Plot of Bulk Fluid Temperature and Crude Glycerol Conversion along the radius of the reactor with a feed temperature of 773K and W/FA0 of 76.47 g cat min/mol C at a depth of 12 mm from the inlet of reactor
The shape of the radial profiles appears flat until the wall of the reactor is approached, where the external temperature is assumed constant, is reached. This can indicate that plug flow is not guaranteed, despite the plug flow criterion proposed in literature as there is a decrease in temperature and conversion at the wall.

Figure 4-9 shows another viewpoint of the effect of the axial dispersion by showing the impact on yield.
Figure 4.9 Effect of Axial Dispersion on Yield on the yield at the end of the reactor at (1) $T_0$ of 773 K and $W/F_A$ of 12.71 g cat min/mol C, (2) $T_0$ of 773 K and $W/F_A$ of 76.47 g cat min/mol C, (3) $T_0$ of 923 K and $W/F_A$ of 12.71 g cat min/mol C, (4) $T_0$ of 923 K and $W/F_A$ of 76.47 g cat min/mol C
Under these four different scenarios, the maximum deviation observed for predicted H₂ yield defined as the ratio of the moles of H₂ produced to the moles of crude glycerol fed to the reactor at the output of the reactor was 2.6%, making the axial term negligible with its impact on yield.

The axial terms are second order and although they add to the effect of both mass and heat in the reactor, their effect may be minimal. Despite this, axial dispersion was included in the models developed in this work for two main reasons. Firstly, there was no excessive computational demand when running the solver, after inclusion of these terms. This has been discussed in previous models as it posed an issue for convergence before the advent of more robust computer processors. Also, although the L/dₒ ratio criterion for negligence of the axial terms was met, the ratio for this model were close to the limit, and could possibly affect the prediction (Windes, 1986; Young & Finlayson, 1973). Despite the correlations used from literature and simulations, it is ideal that the effect of axial dispersion should be determined experimentally.

### 4.4 EFFECT OF TEMPERATURE AND W/Fₐ₀ ON H₂ YIELD

When operating a packed bed tubular reactor, it is important to determine the optimum conditions for maximizing yield of desired products, minimizing coking within the reactor, which shortens the ‘life’ of the catalyst, and ensuring a safe operation which can be caused by thermal runaway (Fogler, 2011). The space time W/Fₐ₀, which is also referred to in industry as the ‘residence time’ is one parameter that can be adjusted to increase conversion of reactants and hydrogen yield in the reactor. Two approaches to increase residence time of a species in a reactor can be to increase the weight of the
catalyst in the reactor, by adding more catalyst material, providing more surface area for the species to react; also by reducing the feed to the reactor which reduces the number of molecules inside the reactor which allows more contact with the catalyst. Space time in the experiments performed by Abdul Ghani (2014) was varied by changing the weight of the catalyst between 0-0.25g. Figure 4-10 shows the predicted yield at the reactor output for varying inlet temperatures and space times with a steam to carbon ratio of 2.6. The heat of reaction used in this solution incorporated the main components of the crude glycerol makeup for the experiments. What is shown here that the increase in temperature at the feed will eventually result in an increase in H₂ yield. It is also shown that the H₂ yield increases with an increase in W/Fₐ₀.
Figure 4-10 Effect of Temperature of H₂ Yield at different W/Fₐ₀
The increase in H\textsubscript{2} yield in these scenarios corresponds to an increase in conversion. As shown in Figure 4-11, at the feed temperature of 773K, with a higher space time, the conversion of the reactor will increase with conversions of 37\%, 60\%, 71\% and 76\%. With the higher space times, there is more contact between reactant molecules and the catalyst bed to incite greater reaction rates, higher crude glycerol conversion rates and H\textsubscript{2} yield for this system.
Figure 4-11 Crude Glycerol Conversion along the length of the reactor with a feed temperature of 773K at a W/FA0 range from 12.71- 101.94 g cat min/mol C
Figure 4-12 Bulk Fluid Temperature along the length of the reactor with a feed temperature of 773K at a W/FA0 range from 12.71- 101.94 g cat min/mol C
According to the simulation, at the maximum space time a temperature of 852°C, is reached at approximately 15 mm along the length of the reactor. At the outlet of the reactor, the temperature reduces after the reaction zone by approximately 20°C. Similar behavior was observed by Halabi et al. (2008) and Ding et al. (2008) when modelling an auto-thermal operation for methane. At the beginning as the reactants flow along the tube, oxidation is more dominant, causing the steep rise in temperature where after the reaction zone, the endothermic reaction takes over in the system, causing the reduction in temperature as components in the reactor moves toward the end of the reactor.

Figure 4-13 and Figure 4-14 shows that with the increase in the feed temperature 873K, similar behavior is obtained with conversion and temperature, however, the reaction zone occurs at a closer distance from the inlet of the reactor. For the maximum space time of 101.94 g min/mol C, the reaction zone occurs at approximately 8 mm upon entering the bed of the reactor. This also indicates that the increase in temperature results in higher conversion of crude glycerol as the reaction rate increases.
Figure 4.13 Crude Glycerol Conversion along the length of the reactor with a feed temperature of 873K at a W/FA0 range from 12.71-101.94 g cat min/mol C
Figure 4.14 Temperature along the length of the reactor with a feed temperature of 873K at a W/FA0 range from 12.71-101.94 g cat min/mol C
Although higher conversions were reached for a higher feed temperature, the higher temperature may not be desired due to coke formation which contributes to catalyst deactivation.

4.5 EFFECT OF THE PELLET SIZE ON EFFECTIVENESS FACTOR

Kinetic experiments are usually performed in scenarios without mass and heat transport limitations, as it has been shown that the pellet size can affect the reaction rate in the reactor (Froment, De Wilde, & Bischoff, 2011). Simulations with the kinetic experiments show that there were very small gradients for concentration and temperature for particles. The effectiveness factor as shown in Figure 4-15 approximates close to 1 indicates that the reaction rates within the particle are close to that on the surface of the catalyst. This is partially attributed to the pellet size of 0.8mm which was chosen in experiments by Abdul Ghani (2014) to eliminate the resistance to mass and heat transfer during the process.
Figure 4-15 Effectiveness Factor along the length of the reactor at different feed temperatures with a pellet diameter of 0.8mm and space time of 76.47 gcat min/mol C,
In conjunction with the effectiveness factor discussed at conditions given in the previous section, we can highlight the concentration and temperature profiles to see the effect of the resistance. Figure 4-16 shows the concentration profiles for the three reactants synthetic crude glycerol, O₂, steam, and the main product H₂. The heterogeneous model showing the bulk fluid and catalyst concentration are compared against a previously built pseudo-homogeneous model. The profiles are generated for a particle size of 0.8 mm and a feed temperature of 873K. For the concentration along the axial length of the reactor, what is shown below is that at the beginning of the process, there is a very small difference between that of solid and fluid until the reaction zone is reached where the two trends converge. With the smaller pellet size, the boundary layer surrounding the pellet is reduced promoting transfer of heat and mass into the pellet, giving a value of η closer to 1. A similar observation is made as well for the temperature.
Figure 4-16 Concentration Profile along the length of the reactor for Crude Glycerol, Oxygen, Steam and Hydrogen for a spherical pellet diameter of 0.8mm at a feed temperature of 873K and W/FA0 of 76.47 gcat min/ mol C
Figure 4-17 Temperature Profile along the length of the reactor a spherical pellet diameter of 0.8mm at a feed temperature of 873K and W/FA0 of 76.47 gcat min/mol C
As shown in Figure 4-18, under similar conditions of temperature, the pellet size is increased to 3.8mm and 6.8mm to observe the results. As shown in previous research by Rúa et al. (2016) for the steam reforming of glycerol, the conversion and temperature distribution profiles along the length of the reactor can be impacted. The effectiveness factor in this simulation for the ATR of glycerol is significantly lower as the pellet size increases with averages of 0.98, 0.70, and 0.46 for pellet sizes of 0.8 mm, 3.8 and 6.8 mm respectively, which indicates that the rate of reaction is impacted as components flow along the reactor.
Figure 4-18 Effectiveness Factor along the length of the reactor at different pellet diameters at a feed temperature of 873K and W/FA0 of 76.47 gcat min/ mol C
The larger particles can contribute to the formation of higher resistances in the particle. With the larger particle, the average diffusion rate decreases across the pore which will reduce and impact of mass transfer into the particle, resulting in the larger concentration and temperature gradients between particle and fluid. Because of the laboratory scale model, there may not be significant effects on the final conversion at the exit of the reactor, but under industrial conditions, different effects can be observed (Rúa & Hernández, 2016).

The two following figures show simulations for a larger pellet size of 3.8 mm which on average will give a smaller estimate effectiveness factor along the length of the reactor. A significant gap exists between the bulk fluid and catalyst with respect to their concentration and temperature before until the reaction zone is reached, which is indicative of increased resistance to heat and mass transfer in the reaction. After the reaction zone, the concentration between the two phases converge after most of the reactants have been consumed.
Figure 4-19 Concentration Profile along the length of the reactor for Crude Glycerol, Oxygen, Steam and Hydrogen for a spherical pellet diameter of 3.8mm at a feed temperature of 873K and W/FA0 of 76.47 gcat min/mol C
Figure 4-20 Temperature Profile along the length of the reactor a spherical pellet diameter of 3.8mm at a feed temperature of 873K and W/FA0 of 76.47 gcat min/mol C
The temperature difference between the two phases is predicted to be approximately 25°C higher in the reaction zone with a larger pellet size. The large temperature difference between the two phases may not be desired as it relates to safety concerns in the reactor. While the conversion of the reactants is not impacted at these inlet conditions, the higher temperature predicted for the temperature of the catalyst can be concerning. With a PBTR operation, it proves beneficial to select the optimum particle size to increase efficiency of the process. The importance of selecting the right size catalyst is important as the simulation shows that the increase in temperature can become an operational hazard.

4.6 INDUSTRIAL SCALE STUDIES

With kinetic data, and simulations performed on laboratory scale dimensions, we can attempt to scale up to industrial conditions. By scaling up we are translating the same product quality derived in initial simulation to a larger unit more tailored towards mass production. There are three methods described by Nauman (2008) for increasing reactor load:

1. Parallel configuration, where capacity is increased by leaving the reactor tube the same size and replicating the tubes in a shell and tube heat exchanger design.
2. Increasing the tube length leaving the diameter of the reactor the same.
3. Increasing the tube diameter to maintain a length to tube diameter ratio for maintaining pressure drop.

These three principles are used in accordance with a scaling factors to produce an upgraded reactor with the same residence time and exit conversions. Simulations have
also been performed with a ‘blind’ approach which produces acceptable quality products (MacDonald, 2014).

A hypothetical industrial reactor is proposed in this work, with dimensions similar to those used for already existent industrial reformers. Currently, there is no existing industrial reforming process for the ATR of crude glycerol, which was the basis of the original results. The hypothesized reactor was simulated to be a single tube as if it were present in multi-tubular reactor. The initial run data for this simulation was given below with main differences being the length of 3m, the diameter of the tube being 58 mm and the spherical catalyst particle with a diameter being 10.8 mm.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Definition and units</th>
<th>Values</th>
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</thead>
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<tr>
<td>$\lambda_{er}^*$</td>
<td>Effective Gas Radial Conductivity, W/m-K</td>
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<tr>
<td>$\lambda_{ez}^*$</td>
<td>Effective Gas Axial Conductivity, W/m-K</td>
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<tr>
<td>$a_v$</td>
<td>Particle surface area to volume ratio, m$^2$/m$^3$</td>
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<tr>
<td>$C_{pr}^*$</td>
<td>Heat capacity, J/kg-K</td>
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</tr>
<tr>
<td>$D$</td>
<td>Internal reactor diameter, mm</td>
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</tr>
<tr>
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<td>Effective Gas Radial Diffusivity, m$^2$/s</td>
<td>$4.11 \times 10^{-3}$</td>
</tr>
<tr>
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<td>Effective Gas Axial Diffusivity, m$^2$/s</td>
<td>$2.71 \times 10^{-2}$</td>
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<td>$d_p$</td>
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<td>$T_a$</td>
<td>External Environmental temperature, K</td>
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<td>Heat transfer coefficient, W/m$^2$ 6C</td>
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<td>$\mu^*$</td>
<td>Viscosity, Pa s</td>
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<tr>
<td>$\rho_g$</td>
<td>Gas Density, kg/m$^3$</td>
<td>0.388</td>
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</table>
4.6.1 PRESSURE DROP IN THE PBTR

For an industrial reactor operation, the pressure drop in the reactor is an important parameter because it affects the operating costs when it comes to pumping and compression (Ghouse & Adams, 2013; MacDonald, 2014). Pressure drop in a packed bed, which was not measured for the system being modelled can be validated by the Ergun equation, given in Chapter 3. To validate this equation for our simulations, experimental data from Pešić et al. (2015) measured the friction factor was varied against Reynolds Number for packed bed with spherical particles of different diameters.
Figure 4-21 Comparison of calculated friction factor using the Ergun equation validated against experimental data from literature (Pešić et al., 2015).
The Reynolds Number was calculated and validated against the data given in the literature and found it acceptable. From literature, a maximum 10% reduction in pressure is desired when flow through the reactor (Nauman, 2008).

Using the Ergun equation for the laboratory scale simulation, the pressure drop was calculated to be 0.14% but may be more significant for a larger reactor.

### 4.6.2 EFFECT OF \( W/F_{A0} \) ON CRUDE GLYCEROL CONVERSION AND TEMPERATURE IN A HYPOTHETICAL INDUSTRIAL REACTOR

Increasing the feed rate is important when considering the operating costs and as shown in Figure 4-22, the higher feed results can impact the reaction zone. The lower reaction zone temperatures are attributed to an increase in the heat removal rate. The reaction zone temperature is also shifted away from the inlet of the reactor causing a higher temperature at the reactor outlet. The increase in flow rate will lower the give a lower conversion at the end of the reactor as shown in Figure 4-23. The trend for the lowest space time is still given an upward trend at the end of the reactor, which would indicate that a longer reactor length would be required to achieve the same conversion at the lower space time.
Figure 4-22 Effect of W/FA0 on the Temperature in the reactor
Figure 4.23 Effect of W/FA0 on the Conversion in the reactor
For the simulation above, with a length of 3m, the lower space time will give a higher pressure drop. From laboratory experiments with regards to the ATR of crude glycerol, at feed temperatures above 873K, the probability of coking occurring is higher. As the trend shows, maximum conversion is not reached at the end of the reactor, for any of the space times as the slope of the trend is still headed upward. At the higher space time, the temperatures at the reaction zone will tend to occur at a higher temperature, however the higher rate of reaction in an auto-thermal setting with steam and oxygen will result in a lower exit temperature for the reactor. In industry, the pellet sizes will be bigger than the 0.8 mm used in the experiments because of the large pressure drop that would occur, as can be seen in the figure above, the resistance between the two phases are similar, which would prove advantageous for temperature control.

Given the thee space times, the pressure drop across the reactor is estimated in the following tables by a doing a manual calculation using the Ergun equation.
Table 4 -6 Relationship between Space Time and Pressure drop for hypothetical industrial reactor

<table>
<thead>
<tr>
<th>Space Time (g cat min/mol C)</th>
<th>Pressure Drop (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>39.1</td>
</tr>
<tr>
<td>100</td>
<td>10.6</td>
</tr>
<tr>
<td>150</td>
<td>5.1</td>
</tr>
</tbody>
</table>
With an industrial operation, it is important to maximize production, promoting the conversion of crude glycerol and yield of desired products, within limitations of pressure drop, catalyst coking and the safety limits of the reactor. These limitations can increase cost in an industrial operation. The simulations shown here that from a higher flowrate will keep the temperature lower in the reactor, however the pressure drop is significant given the pellet size, as well as the crude glycerol conversion will be lower. Abdul Ghani (2014) suggested conditions in his work for ATR of Crude Glycerol to maximize H₂ yield while minimizing coking of the catalyst. What would be required is a financial assessment that balances the objectives of the reaction process with its limitations.
CHAPTER 5: LIMITATIONS, CONCLUSIONS AND RECOMMENDATIONS

The purpose of this work was to simulate a heterogeneous catalytic process for the ATR of synthetic crude glycerol using the power law rate model obtained from kinetic experiments by Abdul Ghani (2014) for the ATR of synthetic crude glycerol. The model for this simulation was done for two different numerical methods, FDM and FEM, each in a different software platform. The system was modelled as steady state given that for a standalone reactor, reactor parameter setpoints can be constant for long periods of time. In developing the model there were some limitations present.

5.1 LIMITATIONS

- A single thermocouple was used in the experiments to record temperature. The system was modelled as a non-isothermal reactor given that the reaction rate is a function of temperature.
- Transport and physical properties were assumed constant. This could introduce uncertainty in the modelling results. The model validation of exit crude glycerol conversions, however gave acceptable predictions. Given the crude feed was synthetic, it proved difficult to establish temperature dependent correlations for these properties.
- A complete model solution would require the velocity profile, in addition to the heat and mass. The processing power of the computers used for this work limited the development of the complete solution. A constant velocity is a reasonable assumption to produce model (Aboudheir et al., 2006; Akande et al., 2006; Azarpour et al., 2017)
5.2 CONCLUSIONS

2-D heterogeneous models were developed for the ATR of synthetic crude glycerol to produce hydrogen gas: the CHM with FEM in COMSOL Multiphysics and the AHM with FDM in MATLAB. The CHM was based on coupling the pellet and bulk fluid domains through the boundary conditions, while the AHM utilized effectiveness factors based on pellet conditions.

The two models were validated against measured experimental data with acceptable absolute deviations of 7.56% and 6.34% for CHM and AHM respectively. With the deviations being acceptable, subsequent simulations for the PBTR model, except for the effectiveness factors were executed with COMSOL Multiphysics. The custom code gives the user absolute control over customization of the model, as opposed to COMSOL Multiphysics which has a standard set of equations, but it requires much more effort. The custom code does however give an added layer of validation to the software being used a commercial software for a PBTR. In this work, a different configuration in COMSOL Multiphysics was used to determine to solve the energy balance, as was required to produce temperature profiles within the catalyst pellet.

The model also demonstrated the suitability of using the effectiveness factor and its contribution to the determining how the size of the particle can affect the conversion of reactants and temperature within the catalyst. The model was also used to simulate a hypothetical industrial reactor tube within a multi-tubular reactor which had a slightly larger diameter and greater length., however, a broader optimization study, with economic assessment would be required to determine adequate scale up conditions.
Overall, the models proved useful in predicting temperature and concentration variations along the reactor for the ATR process.

5.3 RECOMMENDATIONS

To further develop the modelling work discussed in this work, a more comprehensive experimental setup should be setup. A laboratory scale experiment proved useful for this work, however, a larger reactor closer in size to that of an industrial scale, with enhanced instrumentation would prove more useful. The main purpose of the longer reactor is to determine variations in temperature and concentration of components along the length of the reactor. An example of the experimental setup that would be required is described by Windes (1989). The main feature of this experimental setup is the presence of multiple thermocouples to record temperature and sample ports, where samples are collected and measured along the reactor tube. What this does is provide a better way of validating the mass and energy balance in the model. Along with temperature, concentration can also be recorded along the reactor tube as well. The proposed reactor should have instrumentation to measure pressure drop across the tube.
Figure 5-1 A simplified conceptual diagram proposed to recording temperature and concentration for more comprehensive modelling.
Along with the experimental setup, obtaining a fresh crude feedstock instead of a synthetic feedstock could be used for experiments and compared to previous experimental work. For simulation purposes, temperature dependent correlations transport and physical properties and validated with the suggested enhanced instrumentation. It would prove useful to simulate a transient model in conjunction with simulating a control system for the reactor Although this work done using a numerical solution, an attempt should be made to establish an analytical solution.
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APPENDIX A: CRUDE GLYCEROL COMPONENTS AND MOLECULAR FORMULA

The crude glycerol components for the synthetic crude glycerol used in the original experiments by Abdul Ghani, (2014) is given in the table below.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Amount (mol)</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>Component fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>C₃H₅O₃</td>
<td>0.25518</td>
<td>3</td>
<td>8</td>
<td>3</td>
<td>0.4534252</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₂OH</td>
<td>0.17478</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0.3105638</td>
</tr>
<tr>
<td>2-propanol</td>
<td>C₃H₇O</td>
<td>0.1284</td>
<td>3</td>
<td>8</td>
<td>1</td>
<td>0.2281519</td>
</tr>
<tr>
<td>Potassium palmitate</td>
<td>C₁₆H₃₁KO₂</td>
<td>0.00123</td>
<td>16</td>
<td>31</td>
<td>2</td>
<td>0.0021856</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C₁₅H₂₄O₂</td>
<td>0.0023</td>
<td>18</td>
<td>34</td>
<td>2</td>
<td>0.0040868</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>0.00051</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>0.0009009</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>C₂₅H₄₁O₄</td>
<td>0.00039</td>
<td>20</td>
<td>14</td>
<td>4</td>
<td>0.0006859</td>
</tr>
</tbody>
</table>

**Total** 0.56278  **SUM 1**  2.47935  6.91658  1.91518

Figure A-1  Makeup of Synthetic Crude Glycerol used in ATR experiments
APPENDIX B : Calculation of Molecular Weight and Density of Feed Mixture

Molecular Weight of Feed Mixture, \( M_{\text{avg}} \) [g/mol]:

Mass of Crude Glycerol in Feed [g/mol] (Abdul Ghani, 2014): 69.08

<table>
<thead>
<tr>
<th>Partial Pressure, ( P_p ) (atm)</th>
<th>Molecular weight, ( MW ) (g/mol)</th>
<th>Mole fraction, ( MF ) ( (P_p/P_0) )</th>
<th>( MW \times P_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Glycerol</td>
<td>9.48E-02</td>
<td>69.08</td>
<td>0.0948</td>
</tr>
<tr>
<td>Steam</td>
<td>0.61</td>
<td>18</td>
<td>0.61</td>
</tr>
<tr>
<td>O2</td>
<td>5.87E-02</td>
<td>32</td>
<td>0.0587</td>
</tr>
<tr>
<td>N2</td>
<td>0.23</td>
<td>28</td>
<td>0.23</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Density of Feed Mixture [ kg/m³]:

\[
\rho_f = \frac{P \cdot M_{\text{avg}}}{R_g \cdot T_f}
\]

\[
\rho_f = 0.388 \text{ kg/m}^3
\]
APPENDIX C : PROPERTY CALCULATIONS

The conditions used for the calculations will be given in Table 4.1

Effective Radial Diffusivity in the Gas Phase, $D_{er}[m^2/s]$(He, 2003):

$$D_{er} = \frac{u_d d_p}{7 \times (1 + 19.4 \left( \frac{d_p}{D_t} \right)^2)}$$

$$D_{er} = 2.14 \times 10^{-5} \text{ m}^2/\text{s}$$

Effective Axial Diffusivity in the Gas Phase, $D_{ez}[m^2/s]$(He, 2003):

$$D_{ez} = Q \, d_p \left( 0.5 + \frac{0.38}{N_{RE}} \right) = 8.79 \times 10^{-6} \times 0.0008 \left( 0.5 + \frac{0.38}{0.7597} \right)$$

$$D_{ez} = 5.56 \times 10^{-5} \text{ m}^2/\text{s}$$

Particle Surface Area to volume ratio, $a_v[m^2/m^3]$(Hill & Root, 2014):

$$a_v = \frac{6 \left( 1 - \varepsilon_b \right)}{d_p}$$

where

$$\varepsilon_b = 0.4 + 0.05 \frac{d_p}{d_t} + 0.412 \frac{d_p^2}{d_t} = 0.4032$$

$$a_v = 4476.2 \text{ m}^2/\text{m}^3$$

Effective mass transfer coefficient between solid and gas, $k_{fs}[m/s]$(Ferreira, Costa, & Rodrigues, 1992):

$$k_{fs} = \left( \frac{G}{A_C} \right) / \rho_g \times N_{Sc}^{-0.666} \times j_d$$
\[
N_{\text{Sc}} = \frac{\mu}{\rho_b \times D_{ez}} = 0.6982
\]

\[
N_{\text{Pr}} = \frac{C_p \times \frac{\mu}{\lambda_{\text{eff}}}}{0.359} = 0.9143
\]

\[
k_{fs} = 0.0870 \text{ m/s}
\]

**Effective heat transfer coefficient between solid and gas, } h_{fs} [\text{J/s-m}^2-\text{K}]:**

\[
h_{fs} = \left( \frac{G}{A_C} \right) \times C_p \times N_{pr}^{-0.666} \times j^d
\]

\[
h_{fs} = 56.7 \text{ J/s-m}^2-\text{K}
\]
**Effective Diffusivity into the Particle, $D_{es}[m^2/s]$:**

As free glycerol is the main component of the crude glycerol feed, the other components of the feed mixture were neglected for Particle Effective Diffusivity calculations. These calculations were based on a pressure of 1 atm and Temperature of 773K.

<table>
<thead>
<tr>
<th>Component</th>
<th>Diffusion Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>66.07</td>
</tr>
<tr>
<td>Steam</td>
<td>12.7</td>
</tr>
<tr>
<td>O2</td>
<td>16.6</td>
</tr>
<tr>
<td>N2</td>
<td>17.9</td>
</tr>
<tr>
<td>CH4</td>
<td>24.42</td>
</tr>
<tr>
<td>CO2</td>
<td>26.9</td>
</tr>
<tr>
<td>H2</td>
<td>7.07</td>
</tr>
</tbody>
</table>

The Fuller-Schettler- Giddings correlation is given in Equation (3.73) (Hill & Root, 2014). The following calculations are performed for the Effective Diffusivity of Crude Glycerol into the particle. The Effective Diffusivity for other components will be performed in the custom code.
\[
D_{\text{H}_2\text{O}_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{H}_2\text{O}}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{H}_2\text{O}}} + \frac{1}{(\Sigma V_{\text{CO}})} \right)^{0.5} = 8.544 \times 10^{-5} \text{ m}^2/\text{s}
\]

\[
D_{\text{O}_2_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{O}_2}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{O}_2}} \right)^{0.5} = 6.881 \times 10^{-5} \text{ m}^2/\text{s}
\]

\[
D_{\text{N}_2_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{N}_2}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{N}_2}} \right)^{0.5} = 6.961 \times 10^{-5} \text{ m}^2/\text{s}
\]

\[
D_{\text{CH}_4_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{CH}_4}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{CH}_4}} \right)^{0.5} = 7.467 \times 10^{-5} \text{ m}^2/\text{s}
\]

\[
D_{\text{CO}_2_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{CO}_2}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{CO}_2}} \right)^{0.5} = 5.657 \times 10^{-5} \text{ m}^2/\text{s}
\]

\[
D_{\text{H}_2_{-\text{CG}}} = \frac{10^{-3}T^{1.75}}{P} \left( \frac{1}{M_{\text{H}_2}} + \frac{1}{M_{\text{CG}}} \right)^{0.5} \left( \frac{1}{\Sigma V_{\text{H}_2}} \right)^{0.5} = 5.65 \times 10^{-4} \text{ m}^2/\text{s}
\]

**Stoichiometric Ratios**

\[
\frac{N_{\text{H}_2\text{O}}}{N_{\text{CG}}} = 0.75 \quad \frac{N_{\text{O}_2}}{N_{\text{CG}}} = 0.625
\]

\[
\frac{N_{\text{N}_2}}{N_{\text{CG}}} = 0 \quad \frac{N_{\text{CH}_4}}{N_{\text{CG}}} = -2
\]
\[
\frac{N_{CO_2}}{N_{CG}} = -0.5 \quad \frac{N_{H_2}}{N_{CG}} = -3.25
\]

Multicomponent Diffusion for Crude Glycerol

\[
D_{CG-m} =
\left( \frac{\gamma_{H_2O} \cdot \gamma_{CG}}{D_{H_2O-CG}} \right) \left( \frac{\gamma_{H_2O} \cdot \gamma_{CG}}{D_{N_2-CG}} \right) \left( \frac{\gamma_{H_2O} \cdot \gamma_{CG}}{D_{CH_4-CG}} \right) \left( \frac{\gamma_{H_2O} \cdot \gamma_{CG}}{D_{CO_2-CG}} \right) \left( \frac{\gamma_{H_2O} \cdot \gamma_{CG}}{D_{H_2-CG}} \right)
\]

\[D_{CG,m} = 9.852 \times 10^{-5} \text{ m}^2/\text{s}\]

Tortuosity = 2 (Fogler, 2011)

\[D_{es,CG} = \frac{D_{CG-m} \cdot \varepsilon_s}{\tau} = 1.986 \times 10^{-5} \text{ m}^2/\text{s}\]

**APPENDIX D : HEAT OF REACTION, \(\Delta H_{rx}\)**

The typical ATR reaction for this work is as follows:

\[
C_{2.5}H_7O_2 + 6.5 H_2O + 0.625O_2 \rightarrow 0.5 CH_4 + 2 CO_2 + 3.25 H_2 + 5.75 H_2
\]

The heat of reaction calculation will be simplified in this calculation to derive the heat of reaction at the standard temperature of 298K and standard pressure of 1 atm was calculated as shown in the following table. The components considered for the calculation were glycerol, 2-propanol and oleic acid.

The following table gives a summary of the calculation:
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Heat of formation, kJ/mol at 298 K</th>
<th>Coefficient</th>
<th>( v_i \Delta H_{f,i}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Glycerol</td>
<td>-503.9</td>
<td>1</td>
<td>-503.9</td>
</tr>
<tr>
<td>Steam</td>
<td>-241.8</td>
<td>6.5</td>
<td>-1571.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0</td>
<td>0.625</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>-2075.6</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products</th>
<th>Heat of formation, kJ/mol at 298 K</th>
<th>Coefficient</th>
<th>( v_i \Delta H_{f,i}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>-393.5</td>
<td>2</td>
<td>-787</td>
</tr>
<tr>
<td>CH4</td>
<td>-74.9</td>
<td>0.5</td>
<td>-37.45</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0</td>
<td>3.25</td>
<td>0</td>
</tr>
<tr>
<td>Steam</td>
<td>-241.8</td>
<td>5.75</td>
<td>-1390.35</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>-2214.8</strong></td>
</tr>
</tbody>
</table>

\[
\Delta H_{\text{rxn}}^0 = -2214.8 \text{ kJ/mol} - (-2075.6 \text{ kJ/mol}) = -139.2 \text{ kJ/mol}
\]
APPENDIX E: PRESSURE DROP DATA

The pressure drop data for validation of the Ergun equation was extracted from experiments done by (Pešić et al., 2015) as given in the figure below. Data was extracted using the open-source software ‘Digitizeit’.

![Figure E-1](image)

Figure E-1  Experimental data for relationship between the Friction factor $f_p$ vs Reynolds Number $Re_p$ (Pešić et al., 2015)
APPENDIX F: MODEL VALIDATION WITH DATA FROM LITERATURE

Based on the new configuration in COMSOL described in Section 3.3.2.1 being used for this modelling work, another test for validation was to simulate the configuration on data found in literature. A 2-D heterogeneous model for the partial oxidation of ethylene under industrial conditions in a 12 ft long reactor built by Iordanidi, (2002). The data, which was detailed in the dissertation for their model was obtained from Westerterp et al., (1984). The reactions for this process is as follows:

\[ \text{O}_2 + 2 \text{C}_2\text{H}_4 \rightarrow 2 \text{C}_2\text{H}_4\text{O} \quad \Delta H_{rx} = 210 \text{ kJ/mol} \]  \hspace{1cm} (1)

\[ \text{O}_2 + 2 \text{C}_2\text{H}_4 \rightarrow \frac{1}{3} \text{CO}_2 + \frac{2}{3} \text{H}_2\text{O} \quad \Delta H_{rx} = 473 \text{ kJ/mol} \]  \hspace{1cm} (2)

From the trends shown below a good agreement was observed between the trends derived by Iordanidi (2002) and that which was done for this work using the proposed model configuration in COMSOL.
Figure F-2  Temperature and C2H4O Concentration for 2-D heterogeneous model built by Iordanidi (2002)
APPENDIX G: MODEL CODES

% (1) This program is written to perform the following:
% A heterogeneous PBR model for the ATR of Crude Glycerol
% They are solved with the finite difference method in cylindrical geometry.

clear all

close all

global alphap betap gammap Pem Peh Ps Damk Biot tsurr ngrid delr delr2 rad radp

global kgd hmd v1 v2 v3 v4 v5 v6 v7 Beta_0 P0 T0 tfavg Pinit Tinit Beta_dim gridpt

global N_Re N_Fr voidc dr2 dr Pezm neta Pezh eta

P0 = 101325;    % Pa   Feed Pressure
Pr = 1 ;        % atm  Feed Pressure in atm (For catalyst)
T0 = 773;       % K    Inlet Temperature to process
visc= 0.00003;  % Pa.s
Rg = 8.314;     % J/(mol.K) Universal Gas Constant
Ea = 93700 ;    % J/mol Activation Energy
yCG0 = 0.0948;  % Inlet Crude Glycerol Mole Fraction
ySTEAM0 = 0.61; % Inlet Steam Mole Fraction
yO20 = 0.0587;  % Inlet Oxygen Mole Fraction
yN20 = 0.23;    % Inlet Nitrogen Mole Fraction
Mave = 26 ;     % Average Molecular Weight

rhog = P0*Mave/(1000*Rg*T0); % kg/m3 Gas Density at In;let
Cp  =1920 ;    % J/kgK  Heat Capacity of Gas
Cps = 800; % J/kgK  Heat Capacity of Solids

conde = 0.063 ; % W/(m.K) Thermal Conductivity of Gas

Ker = condc; % W/(m.K) Thermal Conductivity of Gas(Radial)

Kez = condc; % W/(m.K) Thermal Conductivity of Gas(Axial)

Kers = 0.348; % W/(m.K) Thermal Conductivity of Gas(Radial)

Kezs = 35; % W/(m.K) Thermal Conductivity of Gas(Radial)

Deff = 0.00010619; % m²/s Effective Diffusivity

% REACTOR DIMENSION CALCULATIONS

D = 0.0127; % m Internal Diameter

Lr = 0.045; % m Packed Bed Length

Rad = D/2; % m Reactor Radius

Dp = 0.8E-3; % m Catalyst Particle Diameter

Rp = Dp/2 % m Catalyst Particle Radius

voidb = 0.4+ 0.05*(Dp/D)+ 0.412*(Dp^2/D); % Void fraction(Poristy of bed)

Vp = 4/3*π*Rp^3; % m Volume of Catalyst Particle

W = 0.15E-3; % kg Weight of Catalyst

Vr = π * Rad^2 * Lr; % m³ Volume of Reactor

Npel = Vr*(1-voidb)/Vp; % Number of catalyst pelleTs(i) in Reactor

Mp = W/Npel; % kg Mass of catalyst pellet

rhos = Mp/Vp; % Density of catlyst pellet, kg/m³

rhoB = W/Vr; % Bulk Density of catalyst, kg/m³
voidc = 1 - (rhoB/rhos); % Porosity of Catalyst Pellet

av = (6*(1-voidb))/Dp; % m^2/m^3 external particle surface area per unit reactor

% CALCULATED PARAMETERS

% REACTOR CALCULATIONS

sptime = 96.86; % g.min/mol Space Time
W_FA0 = sptime*60/1000; % kg.s/mol Space Time conversion

pi = 3.14;

Ac = pi*Rad^2; % m^1 Cross-Sectional Area

PCG0 = yCG0*P0; % Pa Inlet CG partial pressure

Psteam0 = ySTEAM0*P0; % Pa Inlet Steam partial pressure

PO20 = yO20*P0; % Pa Inlet Oxygen partial pressure

PN20 = yN20*P0; % Pa Inlet Nitrogen partial pressure

cCG0 = PCG0/(Rg*T0); % mol/m^3 Inlet CG Concentration

csteam0 = Psteam0/(Rg*T0); % Inlet Steam Concentration

cO20 = PO20/(Rg*T0); % mol/m^3 Inlet Oxygen Concentration

cN20 = PN20/(Rg*T0); % mol/m^3 Inlet Nitrogen Concentration

C_tot_feed = cCG0+csteam0+cN20+cO20; % mol/m^3 Concentration of Feed

FCG0 = 0.00196/(60*2.5); % mol/s Inlet CG molar flowrate

Ft0 = FCG0/yCG0; % mol/s Inlet Total molar flowrate

Fsteam0 = ySTEAM0*Ft0; % mol/s Inlet steam molar flowrate
\[ \text{FO20} = yO20 \cdot Ft0; \quad \% \text{ mol/s Inlet Oxygen molar flowrate} \]
\[ \text{FN20} = yN20 \cdot Ft0; \quad \% \text{ mol/s Inlet Nitrogen molar flowrate} \]
\[ Q = Ft0 / \text{ctot}_\text{feed}; \quad \% \text{ m}^3/\text{s Inlet Volumetric Flowrate} \]
\[ G = Q \cdot \rho g; \quad \% \text{ kg/s Inlet Mass flowrate} \]
\[ u_z = Q / A_c; \quad \% \text{ Superficial velocity at in inlet} \]
\[ \text{convf1} = 1 / (2.5 \cdot 60); \quad \% \text{ conversion factor #1} \]
\[ \text{convf2} = (0.0821 \cdot 3 \cdot T0)^{3.5} \% \text{ conversion factor #2} \]
\[ Ts = T0; \quad \% \text{ Temperature of surrounding environment} \]
\[ \text{kn} = k0 \cdot \exp(-Ea / (Rg \cdot T0)) \cdot (c_{CG0}^1 \cdot c_{steam0}^{0.56} \cdot cO20^{1.87}) \cdot \text{convf2} \cdot \rho B; \]
\[ Utw = 16; \quad \% \text{ Wall heat transfer coefficient} \]

% TRANSPORT CORRELATIONS

\[ N_{Re} = D_p \cdot (G / A_c) / \text{visc}; \quad \% \text{ Reynolds Number} \]
\[ N_{Sc} = \text{visc} / (\rho g \cdot D_{eff}); \quad \% \text{ Schmidt Number} \]
\[ N_{Pr} = C_p \cdot \text{visc} / \text{condc}; \quad \% \text{ Prandtl Number} \]
\[ j_d = 0.357 / (\text{voidb} \cdot N_{Re}^{0.359}); \]
\[ D_{ez} = (u_z \cdot D_p) / (7 \cdot (1 + 19.4 \cdot (D_p / D)^2)); \quad \% \text{ m}^2/\text{s Effective Axial Diffusivity} \]
\[ D_{er} = ((G / A_c) / \rho g) \cdot D_p \cdot (0.5 + 0.38 / N_{Re}); \quad \% \text{ m}^2/\text{s Effective Radial Diffusivity} \]
\[ D_{es} = D_{eff} \cdot \text{voidb}/2; \]
\[ k_g = (G / A_c) / \rho g \cdot N_{Sc}^{(-0.666)} \cdot j_d; \quad \% \text{ m/s Effective Mass Transfer coefficient between solid and gas} \]
hf = jd*Cp*(G/Ac)*N_Pr^(-0.666); %J/m^2/s/K Effective Heat Transfer coefficient between solid and gas
N Fr = 70/uz/Rad;

% PRESSURE DROP CALCULATIONS
dp_term1 = ((G/Ac)*(1-voidb))/(rhog*Dp*voidb^3);
dp_term2 = (150*(1-voidb)*visc)/Dp;
dp_term3 = 1.753*(G/Ac);

% STOICHIOMETRIC CALCUALTIONS
% STOCHIOMETRIC COEFFICIENTS
v1 = -1; %CG
v2 = -0.75; %H2O
v3 = -0.625; %O2
v4 = 0; %N2
v5 = 2; %CO2
v6 = 0.5; %CH4
v7 = 3.25; %H2

% INITIAL MOLE FRACTION RATIOS
omCG = yCG0/yCG0;
omH2O = ySTEAM0/yCG0 ;
omO2 = yO20/yCG0 ;
\[ \text{omN2} = \frac{y_{N20}}{y_{CG0}} ; \]
\[ \text{omCO2} = 0 ; \]
\[ \text{omCH4} = 0 ; \]
\[ \text{omH2} = 0 ; \]

\[ \text{ngrid}=17; \ % \text{Number of Grid Points in the Radial Direction} \]

\% DIMENSIONLESS NUMBERS

\[ \text{alphap} = \frac{L_r D_p}{R_{ad}^2} ; \]
\[ \text{neta} = \frac{L_r}{D_p} ; \]
\[ \text{betap} = \frac{\delta H \cdot c_{CG0}}{\rho_{g0} \cdot T_0 \cdot C_{p}} ; \]
\[ \text{gammap} = \frac{E_a}{R_g \cdot T_0} ; \]
\[ \text{Pem} = \frac{D_p \cdot u_z}{D_{er}} ; \]
\[ \text{Pezm} = \frac{D_p \cdot u_z}{D_{ez}} ; \]
\[ \text{Pezh} = \frac{D_p \cdot u_z}{(K_{ez} / (\rho_{g0} \cdot C_p))} ; \]
\[ \text{Peh} = \frac{D_p \cdot u_z}{(K_{er} / (\rho_{g0} \cdot C_p))} ; \]
\[ \text{Pehs} = \frac{D_p \cdot u_z}{(K_{ers} / (\rho_{os} \cdot C_{ps}))} ; \]
\[ \text{Damk} = \frac{k_n \cdot L_r}{u_z} ; \]
\[ \text{Biot} = \frac{U_{tw} \cdot R_{ad}}{\text{condc}} ; \]
\[ \text{tsurr} = \frac{T_s}{T_0} ; \]
\[ \text{kgd} = \frac{k \cdot a v \cdot L_r}{u_z} ; \]
\[ \text{hmd} = \frac{h_f \cdot a v \cdot L_r}{(\rho_{g0} \cdot C_p \cdot u_z)} ; \]
% set the time interval for integration

zspan = [0 1]

options=odeset('RelTol',1.e-12,'AbsTol',1.e-6)

for i=1:ngrid
    ai(1,i) = cCG0/cCG0;
    ai(2,i) = T0/T0;
    ai(16,i) = T0/T0;
    ai(3,i) = csteam0/cCG0;
    ai(4,i) = cO20/cCG0;
    ai(5,i) = cCG0/cCG0;
    ai(6,i) = csteam0/cCG0;
    ai(7,i) = cO20/cCG0;
    ai(8,i) = cN20/cCG0;
    ai(9,i) = 0/cCG0;
    ai(10,i) = 0/cCG0;
    ai(11,i) = 0/cCG0;
    ai(12,i) = cN20/cCG0;
    ai(13,i) = 0/cCG0;
    ai(14,i) = 0/cCG0;
    ai(15,i) = 0/cCG0;
    % Axial dispersion term initialization
    ai(17,i) = 0;

ai(18,i) = 0;
ai(19,i) = 0;
ai(20,i) = 0;
ai(21,i) = 0;
ai(22,i) = 0;
ai(23,i) = 0;
ai(24,i) = 0;
rad(i) = (i-1)/(ngrid-1);
radm(i) = (i-1)/(ngrid-1)*Rad;
end
delr = 1/(ngrid-1);
delr2=delr*delr;

% move variables to one long list
num = 0;
for nvar = 1:24
  for k=1:ngrid
    num=num+1;
    a0(num) = ai(nvar,j);
  end
end
a0

[z,soln] = ode15s('radcalcs',zspan, a0,options);
% move the variables into variable names
num = 0;
for nvar = 1:17
for j=1:ngrid
    num=num+1;
    temp(:,nvar,j) = soln(:,num);
end
end
for j= 1:ngrid
    conc1(:,j) = temp(:,1,j);
    tempf(:,j) = temp(:,2,j);
    conc2(:,j) = temp(:,3,j);
    conc3(:,j) = temp(:,4,j);
    conc4(:,j) = temp(:,8,j);
    conc5(:,j) = temp(:,9,j);
    conc6(:,j) = temp(:,10,j);
    concs1(:,j) = temp(:,5,j);
    concs2(:,j) = temp(:,6,j);
    concs3(:,j) = temp(:,7,j);
    concs4(:,j) = temp(:,12,j);
concs5(:,j) = temp(:,13,j);
concs6(:,j) = temp(:,14,j);
concs7(:,j) = temp(:,15,j);
temps(:,j) = temp(:,16,j);
end

nn = size(conc1);

for i = 1:nn(1)
    for j=1:ngrid
        c1(j) = conc1(i,j);
        tf(j) = tempf(i,j);
        c2(j) = conc2(i,j);
        c3(j) = conc3(i,j);
        c4(j) = conc4(i,j);
        c5(j) = conc5(i,j);
        c6(j) = conc6(i,j);
        c7(j) = conc7(i,j);
        cs1(j) = concs1(i,j);
        cs2(j) = concs2(i,j);
        cs3(j) = concs3(i,j);
        cs4(j) = concs4(i,j);
        cs5(j) = concs5(i,j);
        cs6(j) = concs6(i,j);
        cs7(j) = concs7(i,j);
    end
end
ts(j) = temps(i,j);

end
%
for pt=2:2:ngrid-1
    w(pt) = 4.;
    w(pt+1) = 2.;
end
w(1) = 1;
w(ngrid) = 1;
sum1 = 0.;
sum2 = 0.;
sum3 = 0.;
sum4 = 0.;
sum5 = 0.;
sum6 = 0.;
sum7 = 0.;
sum8 = 0.;
sum9 = 0.;
sum10 = 0.;
sum11 = 0.;
sum12 = 0.;
sum13 = 0.;
sum14 = 0.;
sum15 = 0.;
sum16 = 0.;

for pt=1:ngrid
    sum1 = sum1 + w(pt)*c1(pt)*rad(pt);
    sum2 = sum2 + w(pt)*tf(pt)*rad(pt);
    sum3 = sum3 + w(pt)*c2(pt)*rad(pt);
    sum4 = sum4 + w(pt)*c3(pt)*rad(pt);
    sum5 = sum5 + w(pt)*cs1(pt)*rad(pt);
    sum6 = sum6 + w(pt)*cs2(pt)*rad(pt);
    sum7 = sum7 + w(pt)*cs3(pt)*rad(pt);
    sum8 = sum8 + w(pt)*c4(pt)*rad(pt);
    sum9 = sum9 + w(pt)*c5(pt)*rad(pt);
    sum10 = sum10 + w(pt)*c6(pt)*rad(pt);
    sum11 = sum11 + w(pt)*c7(pt)*rad(pt);
    sum12 = sum12 + w(pt)*cs4(pt)*rad(pt);
    sum13 = sum13 + w(pt)*cs5(pt)*rad(pt);
    sum14 = sum14 + w(pt)*cs6(pt)*rad(pt);
    sum15 = sum15 + w(pt)*cs7(pt)*rad(pt);
    sum16 = sum16 + w(pt)*ts(pt)*rad(pt);
end
\begin{align*}
  c1avg(i) &= 2. \times (\text{delt}/3.)*\text{sum1} \times cCG0; \\
  cs1avg(i) &= 2. \times (\text{delt}/3.)*\text{sum5} \times cCG0; \\
  c2avg(i) &= 2. \times (\text{delt}/3.)*\text{sum3} \times cCG0; \\
  cs2avg(i) &= 2. \times (\text{delt}/3.)*\text{sum6} \times cCG0; \\
  c3avg(i) &= 2. \times (\text{delt}/3.)*\text{sum4} \times cCG0; \\
  cs3avg(i) &= 2. \times (\text{delt}/3.)*\text{sum7} \times cCG0; \\
  c4avg(i) &= 2. \times (\text{delt}/3.)*\text{sum8} \times cCG0; \\
  cs4avg(i) &= 2. \times (\text{delt}/3.)*\text{sum12} \times cCG0; \\
  c5avg(i) &= 2. \times (\text{delt}/3.)*\text{sum9} \times cCG0; \\
  cs5avg(i) &= 2. \times (\text{delt}/3.)*\text{sum13} \times cCG0; \\
  c6avg(i) &= 2. \times (\text{delt}/3.)*\text{sum10} \times cCG0; \\
  cs6avg(i) &= 2. \times (\text{delt}/3.)*\text{sum14} \times cCG0; \\
  c7avg(i) &= 2. \times (\text{delt}/3.)*\text{sum11} \times cCG0; \\
  cs7avg(i) &= 2. \times (\text{delt}/3.)*\text{sum15} \times cCG0; \\
  tfavg(i) &= 2. \times (\text{delt}/3.)*\text{sum2} \times T0; \\
  tsavg(i) &= 2. \times (\text{delt}/3.)*\text{sum16} \times T0; \\
  \% \text{ Conversion} \\
  xCG(i) &= (cCG0 - c1avg(i)) / cCG0 \times 100; \\
  \% \text{ Mole Fraction of products(i) and reactants(i) along the reactor} \\
  C_{\text{total}}(i) &= cs1avg(i) + cs2avg(i) + cs3avg(i) \\
  &\quad + cs4avg(i) + cs5avg(i) + cs6avg(i) \\
  &\quad + cs7avg(i); \\
\end{align*}
\[ y_{\text{CG}}(i) = \frac{c_{1\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{H}_2\text{O}}(i) = \frac{c_{2\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{O}_2}(i) = \frac{c_{3\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{N}_2}(i) = \frac{c_{4\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{CO}_2}(i) = \frac{c_{5\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{CH}_4}(i) = \frac{c_{6\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{H}_2}(i) = \frac{c_{7\text{avg}}(i)}{C_{\text{total}}(i)}; \]
\[ y_{\text{total}} = y_{\text{CG}} + y_{\text{H}_2\text{O}} + y_{\text{O}_2} + y_{\text{N}_2} + y_{\text{CO}_2} + y_{\text{CH}_4} + y_{\text{H}_2}; \]

% Molar Flow
\[ F_{\text{CG}}(i) = F_{\text{CG}0} - \frac{x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ F_{\text{H}_2\text{O}}(i) = F_{\text{steam}0} + \frac{v_2x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ F_{\text{O}_2}(i) = F_{\text{O}_20} + \frac{v_3x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ F_{\text{N}_2}(i) = F_{\text{CG}0}x_{\text{omN}_2}; \]
\[ F_{\text{CO}_2}(i) = \frac{v_5x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ F_{\text{CH}_4}(i) = \frac{v_6x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ F_{\text{H}_2}(i) = \frac{v_7x_{\text{CG}}(i)}{100}F_{\text{CG}0}; \]
\[ X_{\text{CG}1}(i) = \frac{(F_{\text{CG}0} - F_{\text{CG}}(i))}{F_{\text{CG}0}} \times 100; \]
\[ F_{\text{total}} = F_{\text{CG}} + F_{\text{H}_2\text{O}} + F_{\text{O}_2} + F_{\text{N}_2} + F_{\text{CO}_2} + F_{\text{CH}_4} + F_{\text{H}_2}; \]

% Hydrogen Yield
\[ H_2\text{yield}(i) = \frac{F_{\text{H}_2}(i)}{(F_{\text{CG}0} \times 2.5)}; \]
\( z = z*Lr*1000; \)

subplot(2,2,1);

plot(z,c1avg,z,cs1avg, '--', z,c2avg,z,cs2avg, '--', z,c3avg,z,cs3avg, '--', z,c4avg,z,cs4avg, '--', z,c5avg,z,cs5avg, '--', z,c6avg,z,cs6avg, '--', z,c7avg,z,cs7avg, '--')

xlabel('Axial location(m)')

ylabel('Concentration(mol/m^3)')

legend('average concentration','average temperature')

title('Concentration Profile along the length of reactor')


figure;

subplot(2,2,2);

plot(z,tfavg,z,tsavg, '--')

xlabel('Axial location(m)')

ylabel('Temperature(K)')

legend('average concentration','average temperature')

title('Temperature Profile along the length of reactor')


figure;

subplot(2,2,3);

plot(z,xCG)

xlabel('Axial location(m)')

ylabel('Glycerol Conversion(%)')
for i = 1:nn(1)
    Ts(i) = tsavg(i);
    Pellet.cCGs(i) = cs1avg(i);
    Pellet.csteams(i) = cs2avg(i);
    Pellet.cO2s(i) = cs3avg(i);
    Pellet.cN2s(i) = cs4avg(i);
    Pellet.cCO2s(i) = cs5avg(i);
    Pellet.cCH4s(i) = cs6avg(i);
    Pellet.cH2s(i) = cs7avg(i);

    Pellet.yCG(i) = yCG(i);
    Pellet.yH2O(i) = yH2O(i);
    Pellet.yO2(i) = yO2(i);
    Pellet.yN2(i) = yN2(i);
    Pellet.yCO2(i) = yCO2(i);
    Pellet.yCH4(i) = yCH4(i);
    Pellet.yH2(i) = yH2(i);

    % Determination of Effectiveness Factor
    % Diffusivity within the Particles
    % Diffusivity of Components(i)
% Molecular Weight of components(i)

% 1 - CG; 2 - H2O; 3 - O2; 4 - N2; 5 - CH4; 6 - CO2; 7 - H2;

Pellet.MW_CG = 26; % Molecular Weight of Crude Glycerol
Pellet.MW_H2O = 18; % Molecular Weight of Steam
Pellet.MW_O2 = 32; % Molecular Weight of O2
Pellet.MW_N2 = 28; % Molecular Weight of N2
Pellet.MW_CH4 = 16; % Molecular Weight of CH4
Pellet.MW_CO2 = 44; % Molecular Weight of CO2
Pellet.MW_H2 = 2; % Molecular Weight of H2

% Diffusion Volume
Pellet.DV_CG = 66.07; % Diffusion Volume of Crude Glycerol
Pellet.DV_H2O = 12.7; % Diffusion Volume of Steam
Pellet.DV_O2 = 16.6; % Diffusion Volume of O2
Pellet.DV_N2 = 17.9; % Diffusion Volume of N2
Pellet.DV_CH4 = 24.42; % Diffusion Volume of CH4
Pellet.DV_CO2 = 26.9; % Diffusion Volume of CO2
Pellet.DV_H2 = 7.07; % Diffusion Volume of H2

% Define Binary Diffusivities

% -CG Binary Diffusivities
Pellet.D_H2O_CG(i) = Bin_Diff(Pr, Ts(i), Pellet.MW_H2O, Pellet.MW_CG, Pellet.DV_H2O, Pellet.DV_CG);
Pellet.D_O2.CG(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW_O2,Pellet.MW.CG,Pellet.DV_O2,Pellet.DV.CG);

Pellet.D_N2.CG(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW_N2,Pellet.MW.CG,Pellet.DV_N2,Pellet.DV.CG);

Pellet.D_CH4.CG(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.CH4,Pellet.MW.CG,Pellet.DV.CH4,Pellet.DV.CG);

Pellet.D_CO2.CG(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.CO2,Pellet.MW.CG,Pellet.DV.CO2,Pellet.DV.CG);

Pellet.D_H2.CG(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.H2,Pellet.MW.CG,Pellet.DV.H2,Pellet.DV.CG);

% -H2O Binary Diffusivities

Pellet.D_CG.H2O(i) = Pellet.D_H2O.CG(i);

Pellet.D_O2.H2O(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.O2,Pellet.MW.H2O,Pellet.DV.O2,Pellet.DV.H2O);

Pellet.D_N2.H2O(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.N2,Pellet.MW.H2O,Pellet.DV.N2,Pellet.DV.H2O);

Pellet.D_CH4.H2O(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.CH4,Pellet.MW.H2O,Pellet.DV.CH4,Pellet.DV.H2O);

Pellet.D_CO2.H2O(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.CO2,Pellet.MW.H2O,Pellet.DV.CO2,Pellet.DV.H2O);

Pellet.D_H2.H2O(i) =
Bin.Diff(Pr,Ts(i),Pellet.MW.H2,Pellet.MW.H2O,Pellet.DV.H2,Pellet.DV.H2O);

% -O2 Binary Diffusivities
Pellet.D_CG_O2(i) = Pellet.D_O2_CG(i);

Pellet.D_H2O_O2(i) = Pellet.D_O2_H2O(i);

Pellet.D_N2_O2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_N2,Pellet.MW_O2,Pellet.DV_N2,Pellet.DV_O2);

Pellet.D_CH4_O2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_CH4,Pellet.MW_O2,Pellet.DV_CH4,Pellet.DV_O2);

Pellet.D_CO2_O2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_CO2,Pellet.MW_O2,Pellet.DV_CO2,Pellet.DV_O2);

Pellet.D_H2_O2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_H2,Pellet.MW_O2,Pellet.DV_H2,Pellet.DV_O2);

% -N2 Binary Diffusivities

Pellet.D_CG_N2(i) = Pellet.D_N2_CG(i);

Pellet.D_H2O_N2(i) = Pellet.D_N2_H2O(i);

Pellet.D_O2_N2(i) = Pellet.D_N2_O2(i);

Pellet.D_CH4_N2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_CH4,Pellet.MW_N2,Pellet.DV_CH4,Pellet.DV_N2);

Pellet.D_CO2_N2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_CO2,Pellet.MW_N2,Pellet.DV_CO2,Pellet.DV_N2);

Pellet.D_H2_N2(i) = Bin_Diff(Pr,Ts(i),Pellet.MW_H2,Pellet.MW_N2,Pellet.DV_H2,Pellet.DV_N2);

% -CH4 Binary Diffusivities

Pellet.D_CG_CH4(i) = Pellet.D_CH4_CG(i);

Pellet.D_H2O_CH4(i) = Pellet.D_CH4_H2O(i);
Pellet.D_O2_CH4(i) = Pellet.D_CH4_O2(i);

Pellet.D_N2_CH4(i) = Pellet.D_CH4_N2(i);

Pellet.D_CO2_CH4(i) =
Bin_Diff(Pr,Ts(i),Pellet.MW_CO2, Pellet.MW_CH4, Pellet.DV_CO2, Pellet.DV_CH4);

Pellet.D_O2_CO2(i) =
Bin_Diff(Pr,Ts(i),Pellet.MW_H2, Pellet.MW_O2, Pellet.MW_CH4, Pellet.DV_H2, Pellet.DV_O2);

Pellet.D_N2_CO2(i) = Pellet.D_CO2_N2(i);

Pellet.D_CH4_CO2(i) = Pellet.D_CO2_CH4(i);

Pellet.D_H2_CO2(i) =
Bin_Diff(Pr,Ts(i),Pellet.MW_H2, Pellet.MW_CO2, Pellet.DV_H2, Pellet.DV_CO2);

% -H2 Binary Diffusivities

Pellet.D_O2_H2(i) = Pellet.D_H2_O2(i);

Pellet.D_N2_H2(i) = Pellet.D_H2_N2(i);

Pellet.D_CH4_H2(i) = Pellet.D_H2_CH4(i);
\[
\text{Pellet.D\_CO2\_H2}(i) = \text{Pellet.D\_H2\_CO2}(i);
\]

\% Molar Flux Ratios

\% CG

\begin{align*}
\text{Pellet.NH2O\_CG} &= \frac{v_2}{v_1}; \\
\text{Pellet.NO2\_CG} &= \frac{v_3}{v_1}; \\
\text{Pellet.NN2\_CG} &= \frac{v_4}{v_1}; \\
\text{Pellet.NCH4\_CG} &= \frac{v_5}{v_1}; \\
\text{Pellet.NCO2\_CG} &= \frac{v_6}{v_1}; \\
\text{Pellet.NH2\_CG} &= \frac{v_7}{v_1};
\end{align*}

\% H2O

\begin{align*}
\text{NCG\_H2O} &= \frac{v_1}{v_2}; \\
\text{Pellet.NO2\_H2O} &= \frac{v_3}{v_2}; \\
\text{Pellet.NN2\_H2O} &= \frac{v_4}{v_2}; \\
\text{Pellet.NCH4\_H2O} &= \frac{v_5}{v_2}; \\
\text{Pellet.NCO2\_H2O} &= \frac{v_6}{v_2}; \\
\text{Pellet.NH2\_H2O} &= \frac{v_7}{v_2};
\end{align*}

\% O2

\begin{align*}
\text{NCG\_O2} &= \frac{v_1}{v_3}; \\
\text{Pellet.NH2O\_O2} &= \frac{v_2}{v_3}; \\
\text{Pellet.NN2\_O2} &= \frac{v_4}{v_3}; \\
\text{Pellet.NCH4\_O2} &= \frac{v_5}{v_3}; \\
\text{Pellet.NCO2\_O2} &= \frac{v_6}{v_3}; \\
\text{Pellet.NH2\_O2} &= \frac{v_7}{v_3};
\end{align*}

\% N2

\begin{align*}
\text{NCG\_N2} &= 0; \\
\text{Pellet.NH2O\_N2} &= 0; \\
\text{Pellet.NO2\_N2} &= 0; \\
\text{Pellet.NN2\_N2} &= 0; \\
\text{Pellet.NCH4\_N2} &= 0; \\
\text{Pellet.NCO2\_N2} &= 0; \\
\text{Pellet.NH2\_N2} &= 0;
\end{align*}

\% CH4

\begin{align*}
\text{NCG\_CH4} &= \frac{v_1}{v_6}; \\
\text{Pellet.NH2O\_CH4} &= \frac{v_2}{v_6}; \\
\text{Pellet.NO2\_CH4} &= \frac{v_3}{v_6}; \\
\text{Pellet.NN2\_CH4} &= \frac{v_4}{v_6}; \\
\text{Pellet.NCO2\_CH4} &= \frac{v_5}{v_6}; \\
\text{Pellet.NH2\_CH4} &= \frac{v_7}{v_6};
\end{align*}

\% CO2

\begin{align*}
\text{NCG\_CO2} &= \frac{v_1}{v_5}; \\
\text{Pellet.NH2O\_CO2} &= \frac{v_2}{v_5}; \\
\text{Pellet.NO2\_CO2} &= \frac{v_3}{v_5}; \\
\text{Pellet.NN2\_CO2} &= \frac{v_4}{v_5}; \\
\text{Pellet.NCH4\_CO2} &= \frac{v_6}{v_5}; \\
\text{Pellet.NH2\_CO2} &= \frac{v_7}{v_5};
\end{align*}

\% H2

\begin{align*}
\text{NCG\_H2} &= \frac{v_1}{v_7}; \\
\text{Pellet.NH2O\_H2} &= \frac{v_2}{v_7}; \\
\text{Pellet.NO2\_H2} &= \frac{v_3}{v_7}; \\
\text{Pellet.NN2\_H2} &= \frac{v_4}{v_7}; \\
\text{Pellet.NCH4\_H2} &= \frac{v_5}{v_7}; \\
\text{Pellet.NCO2\_H2} &= \frac{v_6}{v_7};
\end{align*}

\% CG_m
DEN(i) = (yH2O(i) - yCG(i).* Pellet.NH2O_CG)./Pellet.D_H2O_CG(i) + (yO2(i) - yCG(i).* Pellet.NO2_CG)./Pellet.D_O2_CG(i) +
(yN2(i) - yCG(i).* Pellet.NN2_CG)./Pellet.D_N2_CG(i) + (yCH4(i) - yCG(i).* Pellet.NCH4_CG)./Pellet.D_CH4_CG(i) +
(yCO2(i) - yCG(i).* Pellet.NCO2_CG)./Pellet.D_CO2_CG(i) + (yH2(i) - yCG(i).* Pellet.NH2_CG)./Pellet.D_H2_CG(i) ;

NUM(i) = 1 - yCG(i)*( Pellet.NH2O_CG + Pellet.NO2_CG + Pellet.NN2_CG + Pellet.NCH4_CG + Pellet.NCO2_CG + Pellet.NH2_CG) ;

Pellet.DCG_m(i) = NUM(i)./DEN(i)

%H2O_m

DEN(i) = (yCG(i) - yH2O(i).* NC_GH2O)./Pellet.D_CG_H2O(i) + (yO2(i) - yH2O(i).* Pellet.NO2_H2O)./Pellet.D_O2_H2O(i) +
(yN2(i) - yH2O(i).* Pellet.NN2_H2O)./Pellet.D_N2_H2O(i) + (yCH4(i) - yH2O(i).* Pellet.NCH4_H2O)./Pellet.D_CH4_H2O(i) +
(yCO2(i) - yH2O(i).* Pellet.NCO2_H2O)./Pellet.D_CO2_H2O(i) + (yH2(i) - yH2O(i).* Pellet.NH2_H2O)./Pellet.D_H2_H2O(i) ;

NUM(i) = 1 - yH2O(i).* (NC_GH2O + Pellet.NO2_H2O + Pellet.NN2_H2O + Pellet.NCH4_H2O + Pellet.NCO2_H2O + Pellet.NH2_H2O) ;

Pellet.DH2O_m(i) = NUM(i)./DEN(i) ;
\%O_2_m

\text{DEN}(i) = (y_{\text{CG}}(i) - y_{\text{O}_2}(i) \cdot N_{\text{CG}O_2})/\text{Pellet.D}_C_{\text{G}_2}(i) + (y_{\text{H}_2O}(i) - y_{\text{O}_2}(i) \cdot N_{\text{H}_2O})/\text{Pellet.D}_H_{\text{H}_2O}(i) ...

+ (y_{\text{N}_2}(i) - y_{\text{O}_2}(i) \cdot N_{\text{N}_2O_2})/\text{Pellet.D}_N_{\text{N}_2O_2}(i) + (y_{\text{CH}_4}(i) - y_{\text{O}_2}(i) \cdot N_{\text{CH}_4O_2})/\text{Pellet.D}_H_{\text{CH}_4O_2}(i) ...

+ (y_{\text{CO}_2}(i) - y_{\text{O}_2}(i) \cdot N_{\text{CO}_2O_2})/\text{Pellet.D}_H_{\text{CO}_2O_2}(i) + (y_{\text{H}_2}(i) - y_{\text{O}_2}(i) \cdot N_{\text{H}_2O_2})/\text{Pellet.D}_H_{\text{H}_2O_2}(i) ;

\text{NUM}(i) = 1 - y_{\text{O}_2}(i) \cdot (N_{\text{CG}O_2} + N_{\text{H}_2O} + N_{\text{N}_2O_2} + N_{\text{N}_2O_2} + N_{\text{CO}_2O_2} + N_{\text{H}_2O_2}) ;

\text{Pellet.DO}_2_{\text{m}(i)} = \text{NUM}(i)/\text{DEN}(i) ;

\%N_2_m

\text{DEN}(i) = (y_{\text{CG}}(i) - y_{\text{N}_2}(i) \cdot N_{\text{CG}N_2})/\text{Pellet.D}_C_{\text{G}_2}(i) + (y_{\text{H}_2O}(i) - y_{\text{N}_2}(i) \cdot N_{\text{H}_2O})/\text{Pellet.D}_H_{\text{H}_2O}(i) ...

+ (y_{\text{O}_2}(i) - y_{\text{N}_2}(i) \cdot N_{\text{NO}_2N_2})/\text{Pellet.D}_O_{\text{O}_2N_2}(i) + (y_{\text{CH}_4}(i) - y_{\text{N}_2}(i) \cdot N_{\text{CH}_4N_2})/\text{Pellet.D}_H_{\text{CH}_4N_2}(i) ...

+ (y_{\text{CO}_2}(i) - y_{\text{N}_2}(i) \cdot N_{\text{CO}_2N_2})/\text{Pellet.D}_H_{\text{CO}_2N_2}(i) + (y_{\text{H}_2}(i) - y_{\text{N}_2}(i) \cdot N_{\text{H}_2N_2})/\text{Pellet.D}_H_{\text{H}_2N_2}(i) ;

\text{NUM}(i) = 1 - y_{\text{N}_2}(i) \cdot (N_{\text{CG}N_2} + N_{\text{H}_2O} + N_{\text{NO}_2N_2} + N_{\text{N}_2O_2} + N_{\text{CH}_4N_2} + N_{\text{CO}_2N_2}) ;

\text{Pellet.DN}_2_{\text{m}(i)} = \text{NUM}(i)/\text{DEN}(i) ;

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%CH4_m

DEN(i) = (yCG(i) - yCH4(i)* NCG_CH4)/Pellet.D_CG_CH4(i) + (yH2O(i) - yCH4(i)* Pellet.NH2O_CH4)/Pellet.D_H2O_CH4(i) ...

+ (yO2(i) - yCH4(i)* Pellet.NO2_CH4)/Pellet.D_O2_CH4(i) + (yN2(i) - yCH4(i)* Pellet.NN2_CH4)/Pellet.D_N2_CH4(i) ...

+ (yCO2(i) - yCH4(i)* Pellet.NCO2_CH4)/Pellet.D_CO2_CH4(i) + (yH2(i) - yCH4(i)* Pellet.NH2_CH4)/Pellet.D_H2_CH4(i) ;

NUM(i) = 1 - yCH4(i)* (NCG_CH4 + Pellet.NH2O_CH4 + Pellet.NO2_CH4 + Pellet.NN2_CH4 + Pellet.NCO2_CH4 + Pellet.NH2_CH4) ;

Pellet.DCH4_m(i) = NUM(i)/DEN(i) ;

%CO2_m

DEN(i) = (yCG(i) - yCO2(i)* NCG_CO2)/Pellet.D_CG_CO2(i) + (yH2O(i) - yCO2(i)* Pellet.NH2O_CO2)/Pellet.D_H2O_CO2(i) ...

+ (yO2(i) - yCO2(i)* Pellet.NO2_CO2)/Pellet.D_O2_CO2(i) + (yN2(i) - yCO2(i)* Pellet.NN2_CO2)/Pellet.D_N2_CO2(i) ...

+ (yCH4(i) - yCO2(i)* Pellet.NCH4_CO2)/Pellet.D_CH4_CO2(i) + (yH2(i) - yCO2(i)* Pellet.NH2_CO2)/Pellet.D_H2_CO2(i) ;

NUM(i) = 1 - yCO2(i)* (NCG_CO2 + Pellet.NH2O_CO2 + Pellet.NO2_CO2 + Pellet.NN2_CO2 + Pellet.NCH4_CO2 + Pellet.NH2_CO2) ;

Pellet.DCO2_m(i) = NUM(i)/DEN(i) ;
DEN(i) = (yCG(i) - yH2(i)* NCG_H2)/Pellet.D_CG_H2(i) + (yH2O(i) - yH2(i)* Pellet.NH2O_H2)/Pellet.D_H2O_H2(i) ...
  + (yO2(i) - yH2(i)* Pellet.NO2_H2)/Pellet.D_O2_H2(i) + (yN2(i) - yH2(i)* Pellet.NN2_H2)/Pellet.D_N2_H2(i) ...
  + (yCH4(i) - yH2(i)* Pellet.NCH4_H2)/Pellet.D_CH4_H2(i) + (yCO2(i) - yH2(i)* Pellet.NCO2_H2)/Pellet.D_CO2_H2(i) ;

NUM(i) = 1 - yH2(i)*( NCG_H2+ Pellet.NH2O_H2 + Pellet.NO2_H2 + Pellet.NN2_H2 + Pellet.NCH4_H2 + Pellet.NCO2_H2) ;

Pellet.DH2_m(i) = NUM(i).DEN(i) ;

Pellet.Deff_CG(i) = Pellet.DCG_m(i)*voidc/2;
Pellet.Deff_H2O(i) = Pellet.DH2O_m(i)*voidc/2;
Pellet.Deff_O2(i) = Pellet.DO2_m(i)*voidc/2;
Pellet.Deff_N2(i) = Pellet.DN2_m(i)*voidc/2;
Pellet.Deff_CH4(i) = Pellet.DCH4_m(i)*voidc/2;
Pellet.Deff_CO2(i) = Pellet.DCO2_m(i)*voidc/2;
Pellet.Deff_H2(i) = Pellet.DH2_m(i)*voidc/2;

%Define Rate of Reaction
kn(i) = k0 * exp(-Ea/(Rg*Ts(i)))
convf(i) = (1/(2.5*60))*((0.0821E-3*Ts(i))^3.5; % Conversion factor

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Pellet.rxnrate_s(i) = kn(i)*convf(i)*Pellet.cCGs(i)*Pellet.csteams(i)^0.5... *Pellet.cO2s(i)^2*rhos*(1-voidc); % Reaction Rate, mol/m^3/s

Pellet.gammats(i) = Ea/(Rg*Ts(i));

Pellet.betaps(i) = (Pellet.Deff_CG(i)*deltaH*Pellet.cCGs(i))/...
    (Kers*Ts(i))

% Define Theiele Modulus
Pellet.phi(i) = Rp * sqrt(Pellet.rxnrate_s(i)/(Pellet.cCGs(i)*Pellet.Deff_CG(i)));
Pellet.phi2(i) = Pellet.phi(i)^2;
end

for i = 1: nn(1)
    % Define Rate of Reaction
    % Define Theiele Modulus
    Pellet.phi(i) = Rp * sqrt(Pellet.rxnrate_s(i)/(Pellet.cCGs(i)*Pellet.Deff_CG(i)));  
    Pellet.phi2(i) = Pellet.phi(i)^2;
    etaf(i) = (3/Pellet.phi(i)^2)*(Pellet.phi(i)*coth(Pellet.phi(i))-
        1)
    gridpt = 18;
    %dr = 1/(gridpt-1);
    %dr2=dr*dr;
    % Define Theiele Modulus
    Pellet.phi(i) = Rp * sqrt(Pellet.rxnrate_s(i)/(Pellet.cCGs(i)*Pellet.Deff_CG(i)));  
    Pellet.phi2(i) = Pellet.phi(i)^2;
end

% Grid Spacing

c1dim(i) = Pellet.cCGs(i)/Pellet.cCGs(i);
c2dim(i) = Pellet.csteams(i)/Pellet.cCGs(i);
c3dim(i) = Pellet.cO2s(i)/Pellet.cCGs(i);
end
gridpt = 18;

dr = 1/(gridpt-1);

dr2=dr*dr;

for i=1:gridpt

radp(i) = (i-1)/(gridpt);
end

grid = [0:dr:1];

% for i = 1:nn(1);

c_init = ones(size(grid));

% set some options flags for fsolve()
options = optimset('LargeScale','off','Jacobian','off');

for i =1:nn(1)
    cp{i} = fsolve(@isocalcs, ...
                  c_init, options, ...
    Pellet.Deff_CG(i), Pellet.Deff_H2O(i),Pellet.Deff_O2(i), grid...
    ,Pellet.cCGs(i),Pellet.csteams(i),Pellet.cO2s(i),Pellet.phi2(i)...
    ,Pellet.gammats(i),Pellet.betaps(i) );

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for i = 1:nn(1)
    cp1{i}=[cp{i},1];
end
for i = 1:nn(1)
    cp1{i} = [cp{i},1]*Pellet.cCGs(i);
    cp2{i} = Pellet.csteams(i) + v2* (Pellet.Deff_CG(i)/Pellet.Deff_H2O(i))*(Pellet.cCGs(i)-cp1{i})
    cp3{i} = Pellet.cO2s(i) +...
           v3* (Pellet.Deff_CG(i)/Pellet.Deff_O2(i))*(Pellet.cCGs(i)-cp1{i})
    cp7{i} = Pellet.cH2s(i) +...
           v7* (Pellet.Deff_CG(i)/Pellet.Deff_H2(i))*(Pellet.cCGs(i)-cp1{i})
    ratecp{i} = cp1{i}.*cp2{i}.^0.5.*cp3{i}.^2*0.6;
end
radp = [radp,1]*Rp;
for ii = 1:nn(1);

%for i = 1: gridpt
eta(ii)= trapz(radp,ratecp{ii}.*4.*pi.*(radp.^2))/...

(4/3*pi*Rp^3*ratecp{ii}(gridpt));
end

figure
plot(radp,cp1{1})
xlabel('Radial position')
ylabel('Concentration\text{<mol/m}^3\text{'})
title('Concentration of CG in Pellet')

figure
plot(z,eta,--,z,etaf)
xlabel('Axial location(m)')
ylabel('Effectiveness Factor')
title('Effectiveness Factor along the reactor')

%This function is used to perform the mass balance in the pellet
function [f,Jac] = isocalcs(c1,Deff_CG,Deff_H2O,Deff_O2,grid...
    ,cCGs, csteams,cO2s,phi2)

global gridpt dr dr2 rad voidc...
    v1 v2 v3 v4 v5 v6 v7
for j=1:gridpt
    radp(j) = (j-1)/(gridpt);
end

% allocate space for vector
% and Jacobian
f = zeros(1,gridpt);
Jac = spalloc(gridpt,gridpt,3*gridpt);

% Inner Grid Points
for j = 2:gridpt-1
    f(j)= f(j) + (c1(j+1)-2*c1(j)+c1(j-1))/dr2 + (2/radp(j))*(c1(j+1)-c1(j-1))/(2.*dr);
end

% First Grid Point
f(1)= f(1) + 6*(c1(2)-c1(1))/dr2;

% Last Grid Point
f(gridpt) = f(gridpt) + (1 - 2*c1(gridpt) + c1(gridpt-1))/dr2 + (2/radp(gridpt))*(1 - c1(gridpt-1))/(2.*dr);

for j = 1:gridpt
    c2(j) = (csteams/cCGs) + v2* (Deff_CG/Deff_H2O)*(c1(j) - 1);
    c3(j) = (cO2s/cCGs) + v3* (Deff_CG/Deff_O2)*(c1(j) - 1);
end
rxn(j) = c1(j)^1.05*c2(j)^0.56*c3(j)^1.87; Reaction rate
f(j) = f(j) + v1* phi2* rxn(j);
end
return;

% (2) This program is written for a pseudo-homogenous model.
% They are solved with the finite difference method in cylindrical geometry.
clear all
close all
global alphap betap gammap Pem Peh Pehs Damk Biot tsurr ngrid delr delr2 rad
global kgd hmd v1 v2 v3 v4 v5 v6 v7 Beta_0 P0 T0 tavg Pinit Tinit Beta_dim N_r

%!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
P0 = 101325; % Pa Feed Pressure
T0 = 873% % K Inlet Temperature to process
visc= 0.00003; % Pa.s
deltaH = - 65.2E3; % kJ/mol Heat of Reaction
Rg = 8.314; % J/(mol.K) Universal Gas Constant
Ea = 93700 ; % J/mol Activation Energy
yCG0 = 0.0948; % Inlet Crude Glycerol Mole Fraction
ySTEAM0 = 0.61; % Inlet Steam Mole Fraction
yO20 = 0.0587; % Inlet Oxygen Mole Fraction
yN20 = 0.23; % Inlet Nitrogen Mole Fraction
Mave = 24.58; % 26 Average Molecular Weight
rhog = 0.388; % kg/m3 Gas Density

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Cp = 1920; % J/kgK Heat Capacity of Gas
Cps = 800; % J/kgK Heat Capacity of Solids
condc = 0.063; % W/(m.K) Thermal Conductivity
Ker = condc;
Kez = condc;
Kers = 0.348;
Kezs = 35;

Deff = 0.00010619; % m^2/s Effective Diffusivity
neff = 1; % Effective ness factor

% REACTOR DIMENSIONS

D = 0.0127; % m Internal Diameter
Lr = 0.045; % m Packed Bed Length
Rad = D/2; % m Reactor Radius
Dp = 0.8E-3; % m Catalyst Particle Diameter
Rp = Dp/2 % m Catalyst Particle Radius
Vp = 4/3 * pi * Rp^3; % m Volume of Catalyst Particle
W = 0.05E-3; % kg Weight of Catalyst
Vr = pi * Rad^2 * Lr; % m^3 Volume of Reactor
Npel = Vr * (1-0.413)/Vp; % Number of catalyst pellets in Reactor
Mp = W/Npel; % Mass of catalyst pellet, kg
rhos = Mp/Vp;  % Density of catalyst pellet, kg/m^3
rhoB = W/Vr ;   % Bulk Density of catalyst, kg/m^3
voidc = 1 - (rhoB/rhos);

%%%%% CALCULATED Parameters %%%%%

sptime = 12.71;       % g.min/mol  Space Time
W_FA0 = sptime*60/1000;       % kg.s/mol      Space Time conversion
pi = 3.14;

Ac = pi*Rad^2;% print*,'Cross-Sectional Area:', Ac
PCG0 = yCG0*P0;% print*,'Inlet CG partial pressure:',Pcg0
Psteam0 = ySTEAM0*P0; %print*,'Inlet Steam partial pressure:',Psteam0
PO20 = yO20*P0; %print*,'Inlet Oxygen partial pressure:',PO20
PN20 = yN20*P0; %print*,'Inlet Nitrogen partial pressure:',PN20
cCG0 = PCG0/(Rg*T0);% print*,'Inlet CG Concentration:',ccg0
csteam0 = Psteam0/(Rg*T0); %print*,'Inlet Steam Concentration:',csteam0
cO20 = PO20/(Rg*T0); %print*,'Inlet Oxygen Concentration:',cO20

cN20 = PN20/(Rg*T0); %print*,'Inlet Nitrogen Concentration:',cN20

Ctot_feed = cCG0+csteam0+cN20+cO20;% print*, 'Concentration of Feed', Ctot_feed

FCG0 = 0.00196/(60*2.5); %print*, 'Inlet CG molar flowrate', FCG0

Ft0 = FCG0/yCG0; % print*, 'Inlet Total molar flowrate', Ft0

Fsteam0 = ySTEAM0*Ft0; % print*, 'Inlet steam molar flowrate', Fsteam0

FO20 = yO20*Ft0; %print*, 'Inlet Oxygen molar flowrate', FO20

FN20 = yN20*Ft0; %print*, 'Inlet Nitrogen molar flowrate', FN20

Q = Ft0/Ctot_feed;% print*, 'Inlet Volumetric Flowrate', Q

G = Q*rhog;% print*, 'Inlet Mass flowrate', G

uz = Q/Ac;% print*, 'Superficial velocity: Assumed-axial', uz

ur = uz;% print*, 'Radial Velocity :assumed', ur

voidb = 0.4+ 0.05*(Dp/D)+ 0.412*(Dp^2/D); % Void fraction of bed

rhoB= W/Vr; % Bulk Density kg/m^3

convf1 = 1/(2.5*60);

convf2 = (0.0821E-3*T0)^3.5

k0 = 2.09E11* convf1;

Ts = T0;

kn = k0*exp(-Ea/(Rg*T0))*(cCG0*csteam0^0.5*cO20^2)*convf2*rhoB ;

Utw = 16;

%!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

% TRANSPORT CORRELATIONS

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%AV = (6*(1-voidb))/Dp;

N_Re = Dp *(G/Ac)/visc; % Reynolds Number

N_Sc = visc/(rhog*Deff); % Schmidt Number

N_Pr = Cp*visc/condc;

jd = 0.357/(voidb * N_Re^0.359);

Dez = 0.0001698%(uz*Dp)/(7*(1+19.4*(Dp/D)^2));

Der = ((G/Ac)/rhog)*Dp*(0.5+0.38/N_Re);

Des = Deff*voidb/2;

kg = (G/Ac)/rhog*N_Sc^(-0.666)*jd;

hf = jd*Cp*(G/Ac)*N_Pr^(-0.666);

%STOICHIOMETRIC CALCUALTIONS

v1 = -1; %CG

v2 = -0.75; %H2O

v3 = -0.625; %O2

v4 = 0; %N2
v5 = 2; \text{ CO2} \\
v6 = 0.5; \text{ CH4} \\
v7 = 3.25; \text{ H2} \\
ngrid= 19; \\

% set parameters 
alphap = Lr*Dp/Rad^2 ; 
betap = deltaH*cCG0/(rhog*T0*Cp); 
gammapp = Ea/Rg/T0; 
Pem = Dp*uz/Der ; 
Peh =Dp*uz/(Ker/(rhog*Cp)); 
Pehs = Dp*uz/(Kers/(rhos*Cps)) 
Damk = kn*Lr/uz; 
Biot = Utw*Rad/condc; 
tsurr = Ts/T0; 
kgd = kg*av*Lr/uz; 
hmd = hf*av*Lr/(rhog*Cp*uz); 

% set the time interval for integration 
zspan = [0 1] 
options=odeset('RelTol',1.e-12,'AbsTol',1.e-6) 

for i=1:ngrid
yi(1,i) = cCG0/cCG0;
yi(2,i) = T0/T0;
yi(3,i) = csteam0/cCG0;
yi(4,i) = cO20/cCG0;
yi(5,i) = cN20/cCG0;
yi(6,i) = 0/cCG0;
yi(7,i) = 0/cCG0;
yi(8,i) = 0/cCG0;

rad(i) = (i-1)/(ngrid-1);
end
delr = 1/(ngrid-1);
delr2=delr*delr;

% move variables to one long list
num = 0;
for nvar = 1:8
    for k=1:ngrid
        num=num+1;
        y0(num) = yi(nvar,j);
    end
end

y0
[z,solution] = ode15s('radcalcs',zspan, y0,options);

% move the variables into variable names
num = 0;
for nvar = 1:8
    for k=1:ngrid
        num=num+1;
        ytemp(:,nvar,j) = solution(:,num);
    end
end
for k=1:ngrid
    conc1(:,j) = ytemp(:,1,j);
    temp(:,j) = ytemp(:,2,j);
    conc2(:,j) = ytemp(:,3,j);
    conc3(:,j) = ytemp(:,4,j);
    conc4(:,j) = ytemp(:,5,j);
    conc5(:,j) = ytemp(:,6,j);
    conc6(:,j) = ytemp(:,7,j);
    conc7(:,j) = ytemp(:,8,j);
end
nn = size(conc1);
for jii = 1:nn(1)
for j=1:ngrid
    c1(j) = conc1(jii,j);
    t(j) = temp(jii,j);
    c2(j) = conc2(jii,j);
    c3(j) = conc3(jii,j);
    c4(j) = conc4(jii,j);
    c5(j) = conc5(jii,j);
    c6(j) = conc6(jii,j);
    c7(j) = conc7(jii,j);
end

% calculate the average conc and temp
% must use an odd number of points
for i=2:2:ngrid-1
    w(i) = 4.;
    w(i+1) = 2.;
end
w(1) = 1;
w(ngrid) = 1;
sum1 = 0.;
sum2 = 0.;
sum3 = 0.;
sum4 = 0.;
sum5 = 0.;
sum6 = 0.;
sum7 = 0.;
sum8 = 0.;

for i=1:ngrid
    sum1 = sum1 + w(i)*c1(i)*rad(i);
    sum2 = sum2 + w(i)*t(i)*rad(i);
    sum3 = sum3 + w(i)*c2(i)*rad(i);
    sum4 = sum4 + w(i)*c3(i)*rad(i);
    sum5 = sum5 + w(i)*c4(i)*rad(i);
    sum6 = sum6 + w(i)*c5(i)*rad(i);
    sum7 = sum7 + w(i)*c6(i)*rad(i);
    sum8 = sum8 + w(i)*c7(i)*rad(i);
end

c1avg(jjj) = 2.*(delr/3.)*sum1*cCG0;
tavg(jjj) = 2.*(delr/3.)*sum2*T0;
c2avg(jjj) = 2.*(delr/3.)*sum3*cCG0;
c3avg(jjj) = 2.*(delr/3.)*sum4*cCG0;
c4avg(jjj) = 2.*(delr/3.)*sum5*cCG0;
c5avg(jjj) = 2.*(delr/3.)*sum6*cCG0;
c6avg(jjj) = 2.*(delr/3.)*sum7*cCG0;
c7avg(jjj) = 2.*(delr/3.)*sum8*cCG0;

% Conversion
xCG(jjj) = (cCG0 - c1avg(jjj))/cCG0*100;
end

z = z*Lr*1000;
subplot(2,2,1);
plot(z,c1avg,z,c2avg,z,c3avg,z,c4avg,z,c5avg,z,c6avg,...
     z,c7avg)
xlabel('Axial location(m)')
ylabel('Concentration(mol/m^3)')
title('Concentration Profile along the length of reactor')

figure;
subplot(2,2,2);
plot(z,tavg)
figure;
subplot(2,2,3);
plot(z,xCG)
xlabel('Axial location(m)')
ylabel('Glycerol Conversion(%)')

title('Glycerol Conversion along the length of reactor')

% This is the function for the finite difference discretization
% This example excludes axial dispersion.

function dudz=radcalcs(z,y)

global alp hap betap gammap Pem Peh Pehs Damk Biot tsurr ngrid delr delr2 rad

global kgd hmd v1 v2 v3 v4 v5 v6 v7 dpt1 dpt2

% move y into variable names
num = 0;
for nvar = 1:8
    for k=1: ngrid
        num=num+1;
        ytemp(nvar,j) = y(num);
    end
end

c1 = ytemp(1,:);
t = ytemp(2,:);
c2 = ytemp(3,:);
c3 = ytemp(4,:);
\[ c_4 = \text{ytemp}(5,:); \]
\[ c_5 = \text{ytemp}(6,:); \]
\[ c_6 = \text{ytemp}(7,:); \]
\[ c_7 = \text{ytemp}(8,:); \]

% j = 1
\[ dudz(1) = 4.\times(\text{c}_1(2) - \text{c}_1(1))/\text{delr}^2; \]
\[ dudz(1+ngrid) = 4.\times(\text{t}(2) - \text{t}(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*2) = 4.\times(\text{c}_2(2) - \text{c}_2(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*3) = 4.\times(\text{c}_3(2) - \text{c}_3(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*4) = 4.\times(\text{c}_4(2) - \text{c}_4(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*5) = 4.\times(\text{c}_5(2) - \text{c}_5(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*6) = 4.\times(\text{c}_6(2) - \text{c}_6(1))/\text{delr}^2; \]
\[ dudz(1+ngrid*7) = 4.\times(\text{c}_7(2) - \text{c}_7(1))/\text{delr}^2; \]

% j = ngrid
\[ dudz(ngrid) = 2.\times(-\text{c}_1(ngrid) + \text{c}_1(ngrid-1))/\text{delr}^2; \]
\[ dudz(2*ngrid) = 2.\times(-\text{t}(ngrid) + \text{t}(ngrid-1) - \text{Biot}\times\text{delr}\times(\text{t}(ngrid) - \text{tsurr}))/\text{delr}^2; \]
\[ dudz(2*ngrid) = dudz(2*ngrid) - \text{Biot}\times(\text{t}(ngrid) - \text{tsurr}); \]
\[ dudz(3*ngrid) = 2.\times(-\text{c}_2(ngrid) + \text{c}_2(ngrid-1))/\text{delr}^2; \]
\[ dudz(4*ngrid) = 2.\times(-\text{c}_3(ngrid) + \text{c}_3(ngrid-1))/\text{delr}^2; \]
\[ dudz(5*ngrid) = 2.\times(-\text{c}_4(ngrid) + \text{c}_4(ngrid-1))/\text{delr}^2; \]
\[ dudz(6*ngrid) = 2.\times(-\text{c}_5(ngrid) + \text{c}_5(ngrid-1))/\text{delr}^2; \]
\[ \frac{dudz}{dr} = \frac{2}{\Delta r^2} \left( -c6(ngrid) + c6(ngrid-1) \right) \]

\[ \frac{dudz}{dr} = \frac{2}{\Delta r^2} \left( -c7(ngrid) + c7(ngrid-1) \right) \]

\[ \text{for } j=2:ngrid-1 \]

\[ \frac{dudz}{dr} = \left( c1(j+1) - 2c1(j) + c1(j-1) \right) / \Delta r^2 + \left( c1(j+1) - c1(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+ngrid) = \left( t(j+1) - 2t(j) + t(j-1) \right) / \Delta r^2 + \left( t(j+1) - t(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+2*ngrid) = \left( c2(j+1) - 2c2(j) + c2(j-1) \right) / \Delta r^2 + \left( c2(j+1) - c2(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+3*ngrid) = \left( c3(j+1) - 2c3(j) + c3(j-1) \right) / \Delta r^2 + \left( c3(j+1) - c3(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+4*ngrid) = \left( c4(j+1) - 2c4(j) + c4(j-1) \right) / \Delta r^2 + \left( c4(j+1) - c4(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+5*ngrid) = \left( c5(j+1) - 2c5(j) + c5(j-1) \right) / \Delta r^2 + \left( c5(j+1) - c5(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+6*ngrid) = \left( c6(j+1) - 2c6(j) + c6(j-1) \right) / \Delta r^2 + \left( c6(j+1) - c6(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \frac{dudz}{dr}(j+7*ngrid) = \left( c7(j+1) - 2c7(j) + c7(j-1) \right) / \Delta r^2 + \left( c7(j+1) - c7(j-1) \right) / (2 \cdot \text{rad}(j) \cdot \Delta r) \]

\[ \text{end} \]

\[ \text{for } j=1:ngrid \]

\[ \frac{dudz}{dr}(j) = (\text{alphap}/\text{Pem}) \cdot \frac{dudz}{dr}(j) \]

\[ \frac{dudz}{dr}(j+ngrid) = (\text{alphap}/\text{Peh}) \cdot \frac{dudz}{dr}(j+ngrid) \]

\[ \frac{dudz}{dr}(j+ngrid*2) = (\text{alphap}/\text{Pem}) \cdot \frac{dudz}{dr}(j+ngrid*2) \]

\[ \frac{dudz}{dr}(j+ngrid*3) = (\text{alphap}/\text{Pem}) \cdot \frac{dudz}{dr}(j+ngrid*3) \]

\[ \frac{dudz}{dr}(j+ngrid*4) = (\text{alphap}/\text{Pem}) \cdot \frac{dudz}{dr}(j+ngrid*4) \]

\[ \frac{dudz}{dr}(j+ngrid*5) = (\text{alphap}/\text{Pem}) \cdot \frac{dudz}{dr}(j+ngrid*5) \]
dudz(j+ngrid*6) = (alphap/Pem)*dudz(j+ngrid*6);
dudz(j+ngrid*7) = (alphap/Pem)*dudz(j+ngrid*7);
end

% next do the reaction terms

for j=1:ngrid
    dudz(j) = dudz(j) + v1*rate1 ;
    dudz(j+ngrid) = dudz(j+ngrid) + betap*v1*rate1 ;
    dudz(j+ngrid*2) = dudz(j+ngrid*2) + v2*rate1 ;
    dudz(j+ngrid*3) = dudz(j+ngrid*3) + v3*rate1 ;
    dudz(j+ngrid*4) = dudz(j+ngrid*4) + v4*rate1 ;
    dudz(j+ngrid*5) = dudz(j+ngrid*5) + v5*rate1 ;
    dudz(j+ngrid*6) = dudz(j+ngrid*6) + v6*rate1 ;
    dudz(j+ngrid*7) = dudz(j+ngrid*7) + v7*rate1 ;
end

dudz = dudz';

return;